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THE ATOMIC WEIGHT OF OXYGEN.

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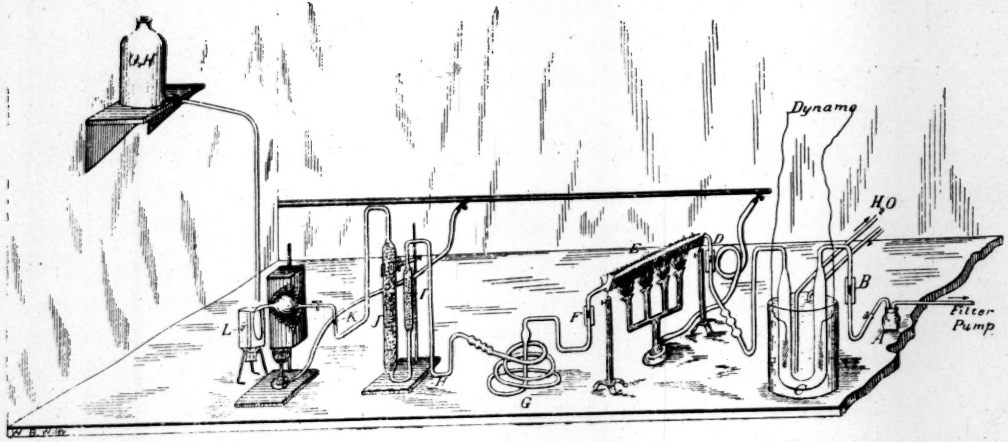
II.

At the conclusion of my first paper[1] the opinion was expressed that the determinations there reported were affected by some source of constant error which had not been discovered. A careful study of all sources of error which I can think of, or which others have been able to suggest, has compelled me, now, to adopt a different conclusion. In view of the further determinations to be described in this paper, and in view of all the experiments which have been tried for the purpose of detecting sources of error, it does not seem to me possible that the *experimental results* of that first series can be in error by more than one part in a thousand. An error in the principle of calculation employed has, however, been detected. In applying the correction for the water obtained by re-oxidising the reduced copper, only *eight-ninths* of the weight of this water was added to the weight of oxygen found. The *total* weight of this water should have been added, since, if all the water could be removed at once, the oxygen found would be greater by the weight of this water and not simply by the weight of the oxygen which it contains. When correctly calculated, the result of this series becomes 15.896. The result of the four series which are now completed does not differ from this by so much as one part in thirty thousand.

[1] This Journal **11**, 155.


U.H
Dynamo
H_2O
L
A
J
I
H
G
F
E
B
Filter
Pump

The hydrogen used in these further determinations has been obtained by the electrolysis of dilute sulphuric acid containing from fifteen to twenty per cent. of the pure acid. The arrangement of the apparatus employed is apparent from the accompanying cut. The voltameter at first used was made for me by Bender and Hobein of Munich. When this was broken by accident, a new one was made by myself. The platinum electrodes were six centimeters by two, and were soldered with gold solder to wire one millimeter in diameter. The solder on the oxygen side was corroded away after a time and the wire was then threaded through the electrode. The distance between the electrodes around the bend of the tube was twelve to fifteen centimeters, and the height of the tube about thirty centimeters. The dynamo used gave a potential of from fifty to sixty volts, and this gave from three to four liters of hydrogen an hour. The current was regulated by a coil of platinum wire immersed in water. By changing the point of contact with this coil the rate of evolution could be instantly changed between quite wide limits and, in this way, suited to the rate of absorption in the copper oxide apparatus. In case of too rapid absorption, the drawing of the acid over into the purifying apparatus could be prevented by attaching a Bunsen pump to the bottle through which the oxygen passed. This was rarely used. In most of the determinations, after connection was once established with the copper oxide apparatus, the hydrogen was passed in continuously, under normal atmospheric pressure, until that part of the experiment was complete.

About 140 cc. of the dilute sulphuric acid were used at first, and when the volume became too small, freshly boiled water was introduced through the tube on the oxygen side. This could be done, of course, without allowing any air to enter the apparatus.

The only impurities which hydrogen generated in such an apparatus can contain are oxygen, ozone, hydrogen dioxide, water, compounds of sulphur, and traces of nitrogen. The first three were removed by passing over heated copper or heated platinised asbestos. The former was used for the determinations of the second series and of the first half of the third series. For the remaining determinations platinised asbestos was used. There seems to be a slight tendency to lower results in these last determinations, but it does not exceed 0.005 H, and I doubt very much if it has any significance. The platinised asbestos would, in the

presence of hydrogen, convert all compounds of sulphur into hydrogen sulphide. The hot copper seems to have the same effect; at least, traces of hydrogen sulphide were apparent from the formation of lead sulphide in the purifying apparatus which followed. The amount of lead sulphide formed was very minute, apparently not exceeding a few milligrams for more than a hundred liters of hydrogen.

Following the asbestos tube is an absorption apparatus containing a solution of fifty parts water, twenty parts caustic potash and two parts of lead sulphate. This was placed in a spiral tube made of tubing of about seven millimeters internal diameter and about four meters in length. The amount of the impurity to be removed from the gas is very small, hence it is a large surface of liquid, rather than a large amount, which should be exposed to its action. Ten or fifteen cc. of the solution is sufficient to keep the walls of such a tube as is described thoroughly moistened, while the capacity of the tube is about 150 cc. At the rate of four liters an hour, any given portion of the gas will take two minutes in passing through it. Dr. C. L. Mees has kindly estimated for me the average number of contacts of the molecules of hydrogen with the walls of a tube of this size in this length of time. He finds that, on the average, each molecule would strike the walls of the tube 600 times in two minutes. The calculation was based on the coefficient of diffusion of hydrogen into itself and on the coefficient of viscosity.

After passing the spiral tube the gas next passed over a few sticks of caustic potash which gradually dissolved in the water brought over from the solution. Next it passed over stick potash and then over phosphorus pentoxide, or, in the third series, over sodium wire.

The joints at the ends of the tube of hard glass containing the copper or the platinised asbestos, were made of rubber tubing covered on the outside with water. On the oxygen side, the connection with a tube dipping under mercury was made in the same way. All other joints were made by sealing the glass. Under an external pressure corresponding to several inches of mercury, the apparatus stood for several weeks without any evidence of leakage. But the best evidence that no leakage occurred is found in the results of the determinations recorded below. In the last series *only 2 cc. of nitrogen were obtained from over sixty liters of hydrogen.*

The apparatus used for the oxidation of the hydrogen has been essentially the same as that described in my first paper. The apparatus has been simplified by bending the side tube for collecting the water downward, instead of making a T connection as in the former apparatus. The apparatus is opened at the end of this tube to introduce the copper oxide and to remove the reduced copper, and, by determining the volume of this tube up to a certain mark, the redetermination of the volume of the apparatus after each experiment becomes unnecessary. For most of the determinations described in this paper the apparatus was blown and the attachment to the stopcock was made by myself. The glass commonly used for "sealing tubes" was employed. The temperature used in my apparatus, as determined somewhat roughly by an air-thermometer, has been about 450°. At this temperature the slighest change in the shape or volume of the bulb was never observed. I was misled by a dealer into the statement that the apparatus used in my first determinations was made of hard glass. Such was not the case.

The connection with the hydrogen apparatus was made by a ground glass joint. After bringing the parts together, the grease in the joint was melted and allowed to solidify. The connection was not again interfered with till the entrance of the hydrogen was complete. This method of connection seems to give almost absolute surety against leakage.

A question of the greatest importance in these determinations is as to how closely the weight of the apparatus can be relied on after heating it for several hours. This was twice carefully tested by heating the vacuous apparatus for three or four hours under the same conditions as those of a determination. After rinsing and wiping the apparatus, there was at first an apparent loss of between one and two milligrams. The next morning the weight was in one case two-tenths, in the other three-tenths of a milligram less than before the heating. A correction of this amount would lower the final value for the atomic weight by about 0.005 H, but I do not feel justified in applying any such correction, and I doubt very much if the error from this source is always in the same direction. In the three series of determinations described in this paper, the weights whose difference gave the weight of the hydrogen were always determined in the morning without opening the balance case, and after the apparatus had

hung on the balance over night. The counterpoise remained on the balance from the beginning to the end of each determination. It is believed that, with the small apparatus which has been used, more is gained by securing constancy in the condition of the apparatus than by attempting to vary the conditions of the apparatus and of the counterpoise in the same way. The volume of the apparatus used has varied from about 80 to 100 cc., and the weight from 130 to 150 grams.

In resuming the work, an attempt was made at first to find some substance which could be used in place of the copper oxide. It was hoped that some substance could be found from which the hydrogen and the water could be expelled without the necessity of a re-oxidation. Lead chromate was at first tried and gave a value of about 15.10. The reduced chromate retained considerable amounts of water which could not be expelled at the temperature used.

Manganese dioxide was next tried. In the first experiment this was heated to dull redness in a copper crucible for some time. This gave the value 16.64. The substance had retained water, both before and after the experiment. A second determination, with manganese dioxide which had been ignited over the blast, gave 15.83. Considerable water was found in the reduced oxide. Later, another determination was made with the ignited oxide, and after expelling the water as far as possible and weighing the apparatus, the reduced oxide was emptied into a combustion tube and the residual water was driven over into a phosphorus pentoxide tube. This gave the value 15.968. Another specimen of the oxide of equal amount, after ignition and heating in the exhausted apparatus in exactly the same manner as in the first part of this last experiment, retained 14 mg. of water which could be driven out by heating in a combustion tube. If a correction of this amount is applied, the value becomes 15.904. I consider this result as of some interest as indicating that my results are not affected to any notable extent by the copper oxide employed. A better guarantee, however, is given by the conduct of the copper oxide itself as described below.

Litharge was also tried, but its action is slow, and in the attempt to hasten it by raising the temperature, using a triple burner, the bulb collapsed.

Returning to the copper oxide, the following method of pro-

cedure was adopted. After expelling the water, as described in my first paper, the heating of the vacuous apparatus was continued for half an hour, the connection with the bulb surrounded with ice being retained. The apparatus was then closed, cooled, and weighed. Dry air was then allowed to enter, the end of the side tube was opened and the copper oxide and reduced copper were transferred quickly to a combustion tube. The latter was always ignited in a current of dry air shortly before use. The copper oxide and metallic copper were then ignited in a current of oxygen, and the water obtained was collected in a phosphorus pentoxide tube. The oxygen was, of course, displaced by dry air before weighing, and a counterpoise of similar volume was used in determining the weights. The correction for the water obtained is much smaller than in the first series, and in the second series it is only one part in a thousand. The smallness of the correction is in part due to a more complete expulsion of the water.

It might be objected that the copper oxide would absorb water in its transference to the combustion tube. This took but a few seconds, but the matter was made the subject of a direct test. The apparatus was filled with copper oxide, heated and exhausted in the usual way. Dry air was then admitted and the copper oxide was transferred to the combustion tube and ignited. Seven-tenths of a milligram of water was obtained. This includes, also, any error which would arise from the retention of water by the copper oxide at the beginning of the experiment. This would correspond to less than 0.002 H in the value of the atomic weight and would tend to raise it.

G. Stillingfleet Johnson[1] has called my attention to the fact that reduced copper retains *water*. I can confirm his statement, but I cannot acknowledge that any considerable error was introduced in my first series from this source. I have carefully read his paper and I find nothing to show that *re-oxidised* copper retains water. On the contrary, he shows that ignition in nitrogen,[2] even, will expel all the water and hydrogen retained by the copper.

To test the retention of water by the reduced copper, the following experiment was tried. After the removal of the water in a determination carried thus far in the usual way, a small amount of dry air was admitted and the apparatus was again weighed. It was then heated and exhausted and the nitrogen obtained was

[1] Chem. News **59**, 272.

[2] J. Chem. Soc. 1879, 242.

measured. The apparatus, also, was cooled and weighed. The loss in weight, less the weight of nitrogen found, gave the weight of the water removed from the apparatus. This was found to be 3.2 mg. It would seem that this must have been nearly or quite all present as *water*, and that it was dislodged from the pores of the reduced copper by heating in the atmosphere of nitrogen. The reduced copper and the copper oxide were then transferred to a combustion tube and the hydrogen and water determined by ignition in a current of oxygen. 1.8 mg. of water was obtained in this way. There were at least 18 to 20 grams of reduced copper in this experiment. When such a weight of copper retains only 0.2 mg. of hydrogen in any form which it will give up at a bright red heat in a current of oxygen, I think no one will claim that, after such ignition, any amount which can affect the determinations can still remain.

Mr. Johnson thinks, also, that the presence of sulphur in my copper oxide may have introduced an error in my work. I find by careful tests an exceedingly minute trace of sulphur, it is true, but I am unable to see how this can affect the results. It is evident that in the removal of the main portion of the water no sulphur can escape. The only chance for error lies then in the amount of water obtained by the re-oxidation of the copper. But this water could be seen to condense in the front part of the tube and afterwards to evaporate at a temperature below the boiling point of water. It is evident, therefore, that it contained no appreciable amount of sulphuric acid. Sulphur dioxide would pass through the phosphorus pentoxide tube unchanged. A further guarantee of the substantial accuracy of the determination of this residual hydrogen and water is the small effect of the correction involved. In the last three series this correction affects the result by about 0.02 H, or about the same as the correction to vacuum in the experiments of Cooke and Richards, or of Keiser, and nearly ten times less than the correction to vacuum by the method of Dumas.

A careful consideration of all sources of error which I can see leads me to believe that there can be no constant error affecting the determination of the weight of the oxygen by more than one or two milligrams, and I think the absolute error is rarely, if ever, greater than that. An error of one milligram affects the result by about 0.002 H.

The question of the trustworthiness of my result resolves itself, then, into a question of the purity of my hydrogen and the accuracy of the determination of its weight. The accuracy of weighing is evident from the agreement among themselves of the determinations of the last two series, taken in connection with the fact that the *conditions of each pair of weighings were as nearly as possible identical.* This last factor is of the greatest importance. By determining the weight before the entrance of the hydrogen with an apparatus which had stood over night, and then determining the weight after the entrance of the hydrogen with an apparatus which had been cooled for several hours, but which had been recently rinsed and wiped, results quite accordant among themselves could be obtained, but the results might be higher than the truth by 0.02 to 0.04 H.

I have sought in every direction which I could think of or which my friends could suggest for evidence of impurities in my hydrogen, but, in every case but one, without success.

Nitrogen was always present, but the amount is very small, and any uncertainty in the amount of the correction to be applied must be entirely insignificant in its effect. It is perhaps conceivable, though very improbable, that ammonia or oxides of nitrogen might be formed. The water obtained was tested with Nessler's reagent with a negative result. The test for nitrous acid with sulphanilic acid and naphthylamine gave in the first case a slight color. A second trial, with greater care to exclude the air, gave no result. Oxides of nitrogen, if formed, might be retained by copper oxide at 450°. Accordingly the copper oxide and reduced copper from one experiment were placed in a combustion tube, which was then connected with the Sprengel pump and exhausted while cold. The mixture was then heated to bright redness for an hour. 0.02 mg. of nitrogen was obtained. In this experiment 0.7 mg. of carbon dioxide was also obtained. Whether this came from a little organic matter or from a trace of calcium carbonate in the copper oxide I cannot say. I do not consider it as practically significant.

Professor Morley has called my attention to the fact that copper oxide sometimes gives off gases slowly when heated in a vacuum. To test this point, the apparatus was filled with copper oxide and the air pumped out as usual. After standing for twenty-four hours it was heated again for four hours and the gases given off

were pumped out and measured. They consisted of 0.039 mg. of carbon dioxide and 0.035 mg. of nitrogen. It seems evident that no error of practical importance arises from this source.

To test for sulphur dioxide, which might pass through the purifying apparatus,[1] ten liters of the hydrogen were passed through a Geissler potash bulb containing a solution of potassium permanganate having one-tenth milligram of available oxygen. The solution retained its color, paling slightly. The loss of color was equally rapid by merely standing in an atmosphere of hydrogen. The solution in the spiral tube of the purifying apparatus, after the passage of 100 liters of hydrogen, showed, when acidified with sulphuric acid, the presence of only an exceedingly minute trace of any substance which would reduce a permanganate solution. The conversion of the sulphur compounds into hydrogen sulphide seems to be, therefore, practically complete.

Professor Morley has suggested to me that carbon in some form might be present in the hydrogen. About nine liters of hydrogen were passed over copper oxide heated in a combustion furnace, and the water formed was condensed in lime water. The latter remained perfectly clear. The water obtained in the determinations was repeatedly tested for carbon dioxide by adding baryta water, and always with negative results. A trace of carbon dioxide was sometimes found in the nitrogen, but only in one case did it exceed one-tenth cc. In that case it was about 0.24 cc. and probably came from the copper oxide, which was from a different source and probably less pure than that used in all the other determinations. In this experiment (the fourth of the last series), the carbon dioxide was left out of the calculation entirely, as it would be without appreciable effect on the weight of the oxygen.

A test for oxygen was made by passing ten liters of hydrogen through a solution of chromous chloride as suggested by v. Pfordten.[2] The result was negative. I do not, however, place much reliance on this test, but am rather disposed to rely on the impossibility that oxygen can pass heated copper, especially in an atmosphere of hydrogen. A more satisfactory test for oxygen would probably be to condense a considerable amount of the hydrogen in palladium and afterwards expel it, causing it to pass through a weighed phosphorus pentoxide tube. Unfortunately I have not been able to apply this test.

[1] Cooke and Richards, this Journal **10**, 98.

[2] Ann. Chem. (Liebig) **228**, 121.

Cooke[1] has recently shown that the efficiency of a phosphorus pentoxide tube may become seriously impaired by use. In the last series more than 100 liters of hydrogen passed through my purifying apparatus, and it was thought wise to test this point, especially as the amount of the drying agent was somewhat less than usual, owing to the difficulty of preparing the sublimed pentoxide which was used. A U-tube with glass stoppers and having the glass tube on one side bent downward and drawn out to fit the socket of my hydrogen apparatus, was filled with phosphorus pentoxide. After passing hydrogen through the tube to displace the air it was closed, noting temperature and pressure, and weighed. A counterpoise of the same size and shape was used. 72 liters of hydrogen were then passed through the tube and it was again weighed. There was absolutely no increase in weight. A decrease of about one-tenth mg. was partly accounted for by change of temperature and pressure. The efficiency of the drying tube is probably due in part to the fact that the gas was almost completely dried by stick potash before it came to the pentoxide tube.

The results of the third and fourth series show that it is possible by my method to distinguish between two specimens of hydrogen, one of which contains less than one-tenth mg. of water per liter, while the other is dry so far as it is possible to say that any gas is dry.

As an illustration, I give here the record in my note-book of one of the determinations of the fourth series.

Volume of apparatus, . . . 79.73 cc.
" " tare, ... 77.35
" " weights, ... 1.83

Tare at 8 A. M. Friday = 15.3335. $t° = 19°.8$, Bar. = 754.
Hydrogen was passed into the apparatus for 2¾ hours.

Tare at 12 M. Friday = 16.1033
" 2 P. M. " = 16.1042
" 8 A. M. Saturday = 16.1042. $t° = 23°.6$, Bar. = 748.
Gain = 0.7707.

The water and gas were expelled.

Tare at 11 A. M. Saturday = 9.2237
" 1 P. M. " = 9.2246.
Loss = 6.1089.

[1] This Journal **11**, 522.

The gas obtained was measured as follows:

V	= 1.9 = 0.615 cc.	Log. $\frac{0.001256}{(1+0.00367t)760}$	$= \bar{6}.18012$
t°	= 25.°		
Bar.	= 748.2	Log. 0.615	$= \bar{1}.78888$
b	= 421.	" 302.4	$= 2.48058$
T	= 23.5	Log. of weight of N	$= \bar{4}.44958$
B′	= 303.7 − 1.3 = 302.4	N	= 0.00028.

After treating with caustic soda the nitrogen remaining was 0.00024.

$$\begin{array}{r} 1.3149 \\ 1.3005 \\ \text{Water by re-oxidation} = 0.0144 \end{array}$$

$$\text{At. W.} = \frac{6.1233 \times 2}{0.7704} = 15.896.$$

I give, next, the more important details of each series, including statements with regard to rejected experiments.

First Series.

This is the series the results of which were published in my first paper. But little need be added to the statements there given. The hydrogen was generated from zinc and hydrochloric acid. Nine experiments in this series were lost or rejected. Three of these were strictly preliminary and precautions afterwards used were omitted. Two were carried no further than the weighing of the hydrogen. In one a little mercury got into the tube through which the hydrogen passed. In one the amount of hydrogen was small, less than two-tenths of a gram, and in one air got into the hydrogen generator. In one sulphuric acid instead of hydrochloric was used to generate the hydrogen. When properly calculated, this last determination becomes 15.890 instead of 15.874, as given in my first paper. (See page 441.)

Second Series.

In this and the succeeding series the hydrogen was obtained by electrolysis as already described. The results of this series are far more discordant than those of any of the other series and contain both the highest and lowest results of all the series. I am not able to give a satisfactory reason for this.

In the first four determinations of the series the hydrogen was dried by a tube filled with phosphorus pentoxide and asbestos,

which had been used for some time. Fearing that this drying tube might have lost its efficiency, it was replaced by a new tube filled with phosphorus pentoxide and having a capacity of about 200 cc. The last two results of the series were obtained with hydrogen dried by this tube and are the lowest of the series, except the fourth, which falls between them. In preparing the sublimed phosphorus pentoxide used in the fourth series it was found that the pentoxide used contained some substance, probably the trioxide, which took fire and burned when heated in a current of oxygen. The presence of a small amount of the trioxide in the large amount of the pentoxide used *may* have caused the low results of these two determinations. I did not feel justified in rejecting them, however, and no determination of any series has been rejected because it gave a high or low result.

Eleven experiments in this series were lost or rejected. In eight of these other substances than copper oxide were used and the results have been described. One was carried only through the weighing of the hydrogen. One was lost by a leakage of the stopcock, and one was made with hydrogen dried by recently distilled sulphuric acid. This last gave the value 15.877.

Third Series.

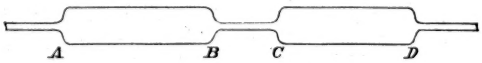
The results of the last two determinations of the second series led me to fear that my hydrogen was contaminated by something coming from the phosphorus pentoxide employed. I determined, therefore, to use a different drying agent and to avoid the use of the pentoxide altogether. A volume of 140 cc. in a large tube was closely packed with sodium wire.

The wire was one half millimeter in diameter and about 20 grams of it were used. This tube was then substituted for the pentoxide tube, the rest of the purifying apparatus remaining essentially unchanged. With hydrogen dried in this way the results of the third series were obtained. Four experiments in this series were lost, three of them by a leakage at some point in the work, and the fourth by reason of a drop of mercury which by some accident got into the side tube and was not discovered till the experiment was nearly completed. The hydrogen was tested by burning from a platinum jet and gave not the faintest sodium color. Indeed, it was with extreme difficulty that the flame could be seen at all in daylight. It was the hydrogen from this apparatus which was tested for carbon with negative results.

The hydrogen from the apparatus was not, however, free from water. Thirty-five to forty liters of the hydrogen were passed through a phosphorus pentoxide tube as described on page 451 and caused a gain in weight of 2 mg. Unfortunately the importance of an accurate determination of the water allowed to pass by the sodium was not realised till after the apparatus was dismantled. There is, therefore, an uncertainty of several liters in the volume of the hydrogen and of a few tenths of a milligram in the weight of water. A correction of 3 mg. is applied to the total hydrogen of this series on account of this water. This raises the result of the series by 0.0096 H. I do not think the uncertainty attaching to the correction can exceed 0.003 H, and I believe that it is less than that.

Fourth Series.

It having been found that the tube of sodium wire does not completely dry the hydrogen passing over it, I determined to return to the phosphorus pentoxide and to make use of a preparation which had been sublimed in a current of oxygen, and which must, therefore, be free from phosphorus trioxide or any substance which could contaminate the hydrogen. A tube consisting of several parts fused together was prepared thus:



At *A*, *B*, *C*, and *D* were placed plugs of asbestos, while the portion from *C* to *D* was filled with phosphorus pentoxide. The tube was then placed in a combustion furnace and the portion from *B* to *C* was heated above the subliming point of the pentoxide. The portion from *C* to *D* was then gradually heated while a current of dry oxygen was passed through the tube. In this way the portion from *B* to *A* was partly filled with the pure pentoxide, free from the trioxide and from phosphoric acid. The tube was then cut off at *C*. Three tubes were filled in this way, and, when sealed together and to the tube filled with stick potash, these formed the drying apparatus used in the last series.

In this series four determinations were lost. Two of these were not completed; in one a little grease was carried away from the

stopcock during the expulsion of the water, and in one the platinised asbestos tube blew out. The experiment last referred to was continued and completed. There was, of course, some diffusion of water, carbon dioxide, nitrogen, and probably of carbon monoxide through the opening. On removal of the gases, about 8 mg. of nitrogen and one milligram of carbon dioxide were found. Supposing the carbon to have entered as carbon monoxide, which seems most probable, and applying the proper corrections, the result of the experiment is 15.892. This shows how perfectly the correction for nitrogen contained in the hydrogen can be applied.

The following summarised statement about the rejected experiments may be of interest. 28 experiments rejected or lost were carried at least as far as the weighing of the hydrogen. 8 of these were lost entirely. 4 of those made with manganese dioxide and lead chromate were grossly in error. Of the remaining 16, fifteen fall between the limits 15.97 and 15.83, and hence show a scarcely greater range than Dumas' best results. The mean of these 15 rejected experiments is 15.892.

The following are the detailed data for the individual series. The probable error of each series is given as the best criterion of the concordance of the results. The calculations have all been carried to the fourth decimal, to avoid, if possible, errors in the third decimal.

First Series.

	Gain.	Loss.	Nitrogen from the hydrogen.	Water by re-oxidation.	Corrected hydrogen.	Corrected oxygen.	Atomic weight.
1	0.9449	7.4785	0.0006	0.0215	0.9443	7.5000	15.885
2	0.6760	5.3521	0.0016	0.0034	0.6744	5.3555	15.882
3	0.7879	6.2432	0.0013	0.0137	0.7866	6.2569	15.909
4	0.5527	4.3483	0.0006	0.0420	0.5521	4.3903	15.904
5	0.4278	3.3366	0.0004	0.0631	0.4274	3.3997	15.909
6	0.8271	6.5437	0.0006	0.0249	0.8265	6.5686	15.895
	4.2164	33.3024	0.0051	0.1686	4.2113	33.4710	95.384

$$\text{Mean} = 15.8973 \pm 0.0032.$$

$$\frac{33.4710 \times 2}{4.2113} = 15.8958.$$

Second Series.

	Gain.	Loss.	Nitrogen from the hydrogen.	Water by re-oxidation.	Corrected hydrogen.	Corrected oxygen.	Atomic weight.
1	0.5054	4.0004	0.0010	0.0091	0.5044	4.0095	15.898
2	0.6328	5.0343	0.0003	0.0042	0.6325	5.0385	15.932
3	0.6356	5.0473	0.0007	0.0044	0.6349	5.0517	15.913
4	0.5576	4.4147	0.0012	0.0028	0.5564	4.4175	15.879
5	0.7339	5.8190	0.0004	0.0034	0.7335	5.8224	15.876
6	0.6706	5.3138	0.0010	0.0043	0.6696	5.3181	15.885
	3.7359	29.6295	0.0046	0.0282	3.7313	29.6577	95.383

Mean = 15.8971 ± 0.0064.

$$\frac{29.6577 \times 2}{3.7313} = 15.8967.$$

Third Series.

	Gain.	Loss.	Nitrogen from the hydrogen.	Water by re-oxidation.	Corrected hydrogen.	Corrected oxygen.	Atomic weight.
1	0.9328	7.4004	0.0005	0.0073	0.9323	7.4077	15.891
2	0.9958	7.8976	0.0006	0.0069	0.9952	7.9045	15.885
3	0.3279	2.5950	0.0011	0.0027	0.3268	2.5977	15.898
4	0.7916	6.2725	0.0009	0.0073	0.7907	6.2798	15.884
5	0.7765	6 1598	0.0003	0.0073	0.7762	6.1671	15.891
6	1.1226	8.8921	0.0005	0.0210	1.1221	8.9131	15.887
	4.9472	39.2699	0.0039	0.0525	4.9433	39.2699	95.336

Mean = 15.8893 ± 0.0014.

Corrected mean = 15.899 (see p. 454).

$$\frac{39.2699 \times 2}{4.9403} = 15.8978 \text{ (see p. 454).}$$

Fourth Series.

	Gain.	Loss.	Nitrogen from the hydrogen.	Water by re-oxidation.	Corrected hydrogen.	Corrected oxygen.	Atomic weight.
1	1.0451	8.2814	0.0007	0.0203	1.0444	8.3017	15.898
2	0.7707	6.1089	0.0003	0.0144	0.7704	6.1233	15.896
3	0.8234	6.5335	0.0003	0.0086	0.8231	6.5421	15.896
4	0.8874	7.0376	0.0002	0.0114	0.8872	7.0490	15.890
5	0.9996	7.9312	0.0003	0.0091	0.9993	7.9403	15.892
6	1.1917	9.4403	0.0007	0.0192	1.1910	9.4595	15.885
	5.7179	45.3329	0.0025	0.0830	5.7154	45.4159	95.357

Mean = 15.8929 ± 0.0013.

$$\frac{45.4159 \times 2}{5.7154} = 15.8925.$$

The mean of all the series, the third series being corrected as already stated, is 15.8965 ± 0.0017. For the last twelve determinations the highest is 15.908 and the lowest 15.885. Ten of these last determinations fall between 15.890 and 15.901.

The result calculated from the sum of the hydrogen and the sum of the oxygen is $\frac{147.8145 \times 2}{18.5983} = 15.8955$.

I accept, therefore, as the most probable value which can be deduced from my work, the number **15.896**. The sources of error which I can see would indicate that the truth lies slightly below rather than above this value, but I do not speak with much confidence on that point.

Meyer and Seubert[1] have not long since expressed the opinion that the value 15.96 does not probably differ from the truth by more than 0.01 H. It seems to me that the facts now at our disposal do not justify such a conclusion. The determinations on which our knowledge of the constant in question rests are the older ones of Dumas, Erdmand and Marchand, and Regnault, and the more recent ones of Cooke and Richards, Lord Rayleigh, Scott, and Keiser. To these may, perhaps, be added determinations by Thomsen, and van der Plaats and the relation of silver to ammonium chloride and ammonium bromide, as found by Stas.

I would not say anything to detract from the esteem which is felt for the laborious and painstaking care with which Dumas conducted his determinations. But Dumas himself said[2] that he should consider himself very fortunate if the future should prove that his result was within one part in two hundred of the truth; that he had striven for an accuracy of one part in a thousand but could not attain it. It has been usually assumed that the errors of his method would tend to give a low rather than a high result. Professor Morley[3] has called my attention to the fact that the hydrogen used by Dumas probably contained carbon from the zinc which he employed. Now, one-tenth mg. of carbon per liter of the hydrogen, if present in the form of a hydrocarbon, would cause the result found to be too high by about 0.05 H. The presence of a given amount of carbon would cause nearly three times as great an error by Dumas' method as by the method used by Cooke or by myself, and the error would be in the opposite direction.

[1] Ber. d. chem. Ges. **22**, 874. [2] Ann. Chim. Phys. 1843, 198. [3] See next article.

Erdmand and Marchand made two series of determinations, one of which gave the value 15.937 and the other 16.01. Unless some valid reason can be given for rejecting one or the other of these series, it is evident that their work leaves a very great uncertainty in the second decimal.

The ratio of densities as found by Regnault and corrected by Crafts[1] is 1 : 15.91. To derive the atomic weight from this we must know the ratio of combination for the gases. Scott[2] has worked carefully on this problem, but the last word that I can find from him is a statement[3] that his earlier determinations were affected by a somewhat serious source of error. From Avogadro's law and the conduct of oxygen and hydrogen under changes of temperature and pressure, it seems probable that the ratio is at least as great as 2 : 1. The question is an experimental one, however, and I hope that we may soon have satisfactory evidence in regard to it. Scott has not determined whether the residual fixed gases of his experiments come from the oxygen or the hydrogen. As Morley[4] has suggested, by the conversion of a part of the hydrogen into water by copper oxide and by the absorption of a part of the oxygen by metallic copper, it is possible to eliminate this uncertainty. Unless the uncertainty can be made very much smaller than it has been, it would seem that this should be done.

Cooke and Richards have obtained the value 15.869. In my first paper the opinion was expressed[5] that the hydrogen used in their determinations must have contained nitrogen. In a more recent paper Cooke[6] still maintains the purity of his hydrogen. While I should be loth to be drawn into any controversy with an investigator of such recognised ability and wide experience, my first statement still seems to me justifiable. The only evidence of the absence of nitrogen furnished in the papers referred to is that derived from the use of the spectroscope. But the evidence of the spectroscope is certainly not trustworthy in such a case until accompanied by some evidence as to the limit of the delicacy of the test when applied to the gases in question. The method which I have used enables me to detect nitrogen when there is only one part in thirty thousand by volume. It would seem desirable that such a test should be applied to the hydrogen furnished by the generator employed by Cooke and Richards.

[1] Compt. Rend. **106**, 1664. [2] Proc. Roy. Soc. **42**, 396. [3] Nature **37** (1888), 439.
[4] This Journal **10**, 23. [5] This Journal **11**, 161. [6] Ibid. **11**, 539.

Lord Rayleigh[1] has obtained the value 15.884 for the ratio of the densities of oxygen and hydrogen. He has also[2] obtained the value 15.89 for the atomic weight as determined by the direct combination of the elements. These results certainly indicate that the results obtained by Regnault and by Cooke and Richards cannot be so wide of the truth as Meyer and Seubert would have us suppose.

Among recent determinations, that of Keiser stands alone as approaching Dumas' value. When Keiser's paper first appeared I believed that the result which he had obtained must be very near the truth and I fully expected to obtain a similar result. After I became convinced by months of labor that the true value must be decidedly lower, I was led to re-examine the paper very carefully and I think there is one serious source of error in the determinations. A phosphorus pentoxide tube was interposed between the palladium and combustion tubes and the gain in weight of this tube was ascribed to water in the hydrogen. But the palladium tube had previously been exhausted and considerable hydrogen had been removed from it while under a very low tension. This should remove any moisture present also, and it would seem that the gain in the pentoxide tube must rather have come from the nitrogen, oxygen and air which also passed through the tube. This would seem the more probable if a few inches of rubber tubing were used for the passage of the gases, as would seem to be indicated by the diagram. Dr. Keiser informs me that without the correction referred to, the value would be between 15.92 and 15.93. There would still be a difference of about 0.025 H between his value and mine. As to this difference I am unable to offer any satisfactory explanation.

Van der Plaats states[3] that by the combustion of known volumes (15 liters) of hydrogen he finds the value 15.94 to 15.96. I am unable to refer to the original paper, but, as the weight of the hydrogen was undoubtedly calculated from the old value obtained by Regnault, a correction must be applied and the value becomes 15.89 to 15.91.

Thomsen's value[4] certainly requires this correction and then becomes 15.91. The amount of hydrogen burned was only one liter, however, in each determination, and the work was not intended as a determination of the atomic weight.

[1] Proc. Roy. Soc. **43**, 356. [2] Ibid. **45**, 425. [3] Ann. Chim. Phys. 1886, **7**, 529.
[4] Ber. d. chem. Ges. **3**, 928.

From the relation of silver to ammonium chloride and ammonium bromide as found by Stas and calculated by van der Plaats, the value 15.885 has been deduced,[1] but considerable uncertainty attaches to some of the data employed.

In conclusion I wish to express my hearty thanks to Professor Morley for the suggestions which have been referred to, and to Mr. W. B. Wiley who made the accompanying drawing.

Rose Polytechnic Institute, *May*, 1890.

CARBON AN IMPURITY IN HYDROGEN AFFECTING DETERMINATIONS OF ITS ATOMIC WEIGHT.

By Edward W. Morley.

It is well known that metals prepared by the usual metallurgic processes contain gases. For instance, platinum or aluminum electrodes in a Plücker tube give off gas on heating by an electric discharge; wires of various metals enclosed in a vacuous space give off gas on heating by an electric current; in making certain castings, founders use artifices to prevent damage from gases remaining in the casting. It is therefore probable that zinc used in preparing hydrogen often contains imprisoned gases, and that hydrogen prepared from it often contains impurities whose nature and amount is of importance in attempting to determine the atomic weight of hydrogen. I published a brief statement of this source of error several years since, in an account of some of my analyses of air;[1] the published accounts of others engaged in determining the atomic weight of hydrogen have not noted the point, although it is well worthy of attention; so that it may not have been sufficiently taken into account.

1. When the purest zinc obtainable from manufacturers of pure chemicals is dissolved in dilute acids, the hydrogen produced usually contains carbon not readily removable by absorption and washing. I have tried many samples of expensive grades of zinc. If copper oxide be long heated in a current of oxygen it ceases to give off carbon dioxide. If then hydrogen be prepared as mentioned, and passed over the heated copper oxide, lime water soon

[1] Brauner, Chem. News **58**, 307.

shows that carbon dioxide is produced. I have not yet obtained any zinc in commerce which failed to give a notable precipitate when ten or twenty liters of hydrogen prepared from it were so treated, and few in which half a liter did not give one.

2. When the purest commercial zinc is amalgamated and hydrogen obtained from it by electrolysis in the Bunsen decomposing cell, or in the modification of it used in my air analyses, and in the determination of the atomic weight of hydrogen by Cooke and by Rayleigh, the hydrogen often contains carbon. This I have proved by experiments like those last mentioned.

3. The purest zinc obtainable in commerce contains gases which are given off on melting it in a vacuum. Dr. W. H. Burton was so kind as to make a few experiments on this point. Such quantities as sixty and seventy grams of zinc, when heated to fusion in a well exhausted glass tube, gave off four or five cubic centimeters of gas. Part was carbon dioxide; after this was removed, explosion with oxygen produced from one-fifth to four-fifths of a cubic centimeter of carbon dioxide: part was nitrogen.

4. Hydrogen produced by the electrolysis of an alkaline hydroxide is likely to contain carbon, unless no alkaline carbonate is present. I tried for some time to obtain pure hydrogen by electrolysis of an alkaline solution. In the last experiment, when about abandoning the attempt for the present, I made a decomposing cell of clean glass and clean platinum, removed traces of organic matter by long treatment with chromic acid, and filled it with a solution of potassium hydroxide and potassium carbonate. When hydrogen was obtained from it by electrolysis and passed over heated pure copper oxide, baryta water was immediately rendered turbid. Unless, therefore, carbonic acid is removed from the alkaline solution in the voltameter, as by the use of barium hydroxide, hydrogen obtained from it cannot be assumed to be free from carbon.

5. It is probable that hydrogen obtained by acting on aluminum with an alkaline hydroxide would contain carbon; so probable that I have laid aside material and apparatus made ready for determinations of atomic weight with such hydrogen; but I have not yet found it worth while to *prove* the presence of such impurity.

6. Hydrochloric acid often contains organic matter; it is conceivable that hydrogen obtained by its use might contain carbon.

Sulphuric acid can be freed from carbon by distillation; but it is not so easy to purify hydrochloric acid if once contaminated. Hence, if one prepare zinc free from carbon by distillation in a vacuum, it may be convenient to use sulphuric acid instead of hydrochloric acid in preparing hydrogen from it. Dr. W. H. Burton has been so good as to prepare for me over a kilogram of zinc free from carbon.

The bearing of these facts on the determination of the atomic weight of hydrogen is obvious. If hydrogen containing carbon is weighed to determine its specific gravity, this will appear too large. If hydrogen containing carbon is weighed and burned, and the water produced is weighed, the atomic weight of hydrogen will appear too large. If hydrogen containing carbon is mixed with oxygen and exploded in the eudiometer, the combining volumes deduced will depend on the assumptions made as to the nature and source of the impurities remaining in the eudiometer. If weighed quantities of hydrogen containing carbon, and of oxygen are combined, oxygen will be wasted in oxidising the carbon, and the true weight of the hydrogen will be uncertain. If copper oxide is heated in a current of hydrogen containing carbon, oxygen will be consumed by the carbon, the carbon dioxide produced will be removed from the water by the prolonged current of hydrogen in which the reduced copper is cooled; so that the hydrogen as determined by difference will appear too small, and its atomic weight will be in defect.

The purity of the hydrogen used in a determination of its atomic weight must be proved, or else the impurity determined and a correction applied. If all impurities but nitrogen are removed, the residual nitrogen can be determined, although with some manipulative difficulty.

Since in a recent determination of the atomic weight of hydrogen it was sought to prove the purity of hydrogen by spectroscopic examination, it may be well to compare the delicacy of spectroscopic indications with that of gas analysis. With the spectroscope Best,[1] making the experiment at the suggestion of Sir Henry Roscoe, could not detect less than 0.011 nitrogen in hydrogen. Eudiometric analysis can detect far less. No very unusual manipulation will detect one part in a thousand; an apparatus permitting fractional explosion will detect and measure one part in ten

[1] Chem. News 55, 209.

thousand if it be provided with a sufficiently accurate means of reading volumes, and if the volumetric composition of water be first determined. And if a liter of hydrogen be passed into a vacuum containing pure hot copper oxide, and so be reduced to a volume of say ten cubic centimeters, then analysed in my eudiometer, it is possible to detect one part of nitrogen in more than one hundred thousand of hydrogen.

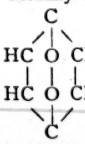
So far, by the electrolysis of dilute sulphuric acid, I have succeeded in obtaining hydrogen at a rate of ten and twenty liters an hour in which there is no carbon, no sulphur, in which, I believe, there is no oxygen, and in which the remaining nitrogen sometimes is too small to be detected by a process which readily detects one-hundredth of a cubic centimeter of nitrogen in a liter of hydrogen, and in which duplicate analyses agree within less than this amount.

Contribution from the Chemical Laboratory of Clark University, Worcester, Mass.

THE CONSTITUTION OF BENZOQUINONE.

By J. U. Nef.

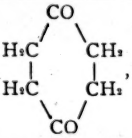
Although a large number of facts have become known concerning quinone and its derivatives, there are no reactions which can be regarded as decisively proving which of the three formulæ that have been put forward as representing the constitution of this substance is actually the correct one. In favor of the hyperoxide formula,



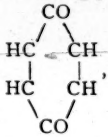
, first advanced by Graebe,[1] is the fact that quinone by reduction takes up two and not four hydrogen atoms in the formation of hydroquinone. Further, the fact that on treatment with phosphorus pentachloride each of the oxygen atoms is replaced by one univalent chlorine atom, with formation of para-dichlorbenzene. Also a number of its properties are in

[1] Ann. Chem. (Liebig) **146**, 3.

favor of this formula. Quinone is a yellow substance, possessing a strong odor resembling chlorine, and it reacts as a powerful oxidising agent; it decomposes, for instance, hydrochloric and hydrobromic acid,[1] taking up the hydrogen and setting free chlorine or bromine. It behaves in this respect like hydrogen peroxide or its organic derivatives benzoyl- and acetyl-hyperoxide. In marked contrast thereto are the properties of para-diketo-

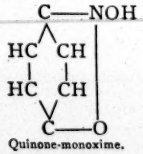


hexamethylene, , which, by reason of the investigation of v. Baeyer and Noyes,[2] is unquestionably to be regarded as a para-diketone. This substance is colorless, reacts with prussic acid and phenylhydrazine, and possesses no oxidising properties.

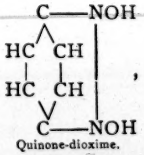
If quinone be regarded as a para-diketone,  , differing therefore from the substance just mentioned only in that it contains four hydrogen atoms less, it is very difficult to give an explanation for the totally different properties of the two compounds.

In favor of the ketone formula for quinone is the fact that it reacts with hydroxylamine, forming, according to Goldschmidt,[3] a monoxime, and, as has been shown by Nietzki and Kehrmann,[4] a dioxime.

Since, however, these oximes can be derived from the hyperoxide formula as follows:



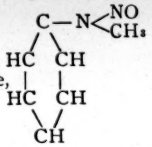
Quinone-monoxime.



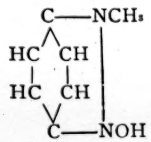
Quinone-dioxime.

[1] Sarauw: Ann. Chem. (Liebig) **209**, 93; Levy and Schultz, ibid. **210**, 233.
[2] Ber. d. chem. Ges. **22**, 2168. [3] Ibid. **17**, 213. [4] Ibid. **20**, 614.

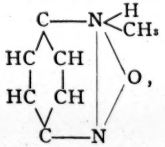
the formation of oximes does not prove the ketone nature of quinone. There are indeed many chemists who regard the fact



that methylaniline-nitrosamine, is converted by means of alcoholic hydrochloric acid into *p*-nitroso-methylaniline,



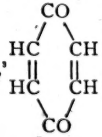
or



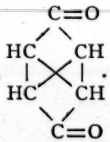
as a proof of the existence of a binding between the two nitrogen atoms in the para position.

The instability of carboxylated derivatives[1] of benzoquinone, as well as also the ready elimination[2] of the halogen atoms in halogen substituted quinones, are points decidedly in favor of the ketone nature of quinone, since genuine benzene derivatives containing the carboxyl or halogen group are exceedingly stable.

Two ketone formulæ for quinone have been put forward; the



first, by Fittig and Siepermann,[3] which assumes the existence of two doubly bound carbon atoms. Later, Claus[4] decided in favor of the existence of two para bonds, and suggested



the following formula,

[1] Ann. Chem. (Liebig) **237**, 17.
[2] Ber. d. chem. Ges. **20**, 2027.
[3] Ann. Chem. (Liebig) **180**, 23.
[4] J. prakt. Chem. [2] **37**, 461.

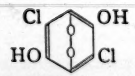
The majority of those who favor the ketone formula of quinone have unquestionably regarded Claus's diagonal formula as the more probable, since up to the present time no facts are known which point in any way to the existence of two doubly bound carbon atoms in quinone, unless perhaps the observation that thymoquinone[1] polymerises in the light.

When one considers, on the other hand, that in the many reduced benzene derivatives there is not one in which a para binding exists, as has been conclusively proved by v. Baeyer's experiments, we have here again a strong argument against Claus's formula. Nietzki,[2] and with him also Claus, assumes that rhodizonic acid has the two hydroxyl groups in the para position, $HOC<\frac{CO-CO}{CO-CO}>COH$, and in that case it must have a para bond. This has, however, not been proved by Nietzki's experiments, and the facts presented in the experimental part of this paper make it improbable that these groups are in the para position.

In order to settle definitely the question concerning the constitution of benzoquinone the study of the anilic acids seemed especially promising, and was begun with this object in view.

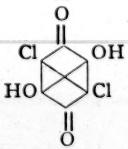
The first point to be determined was whether the two hydrogen atoms in the anilic acids can be removed by oxidation or not. It is necessary to state here that, as has been proved experimentally (see below), the hydrogen atoms in these acids are bound to oxygen, and not to carbon, as I supposed formerly,[3] and that tautomerism is excluded in the anilic acid series. Chloranilic acid is therefore *p*-dichlor-dioxy-quinone, and we have the choice between the following three formulæ:

I.



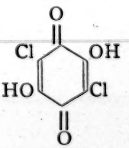
Hyperoxide formula.

II.



Diagonal formula of Claus.

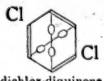
III.



Ketone formula of Fittig.

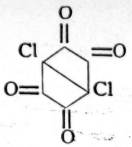
[1] Liebermann, Ber. d. chem. Ges. **10**, 2177; Liebermann and Ilinski, ibid. **18**, 3193.
[2] Ber. d. chem. Ges. **18**, 1842. [3] This Journal **11**, 17.

Assuming formula I or II to be correct, there is no reason why the two hydrogen atoms should not be removed by oxidation. On this supposition the following products would be formed:



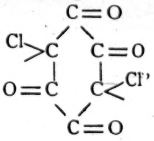
P-dichlor-diquinone hyperoxide formula.

or



P-dichlor-diquinone, Claus's formula.

of which the latter would then represent dichlorrhodizonic acid.

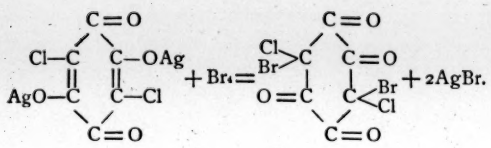
The removal by oxidation of the two hydrogen atoms in chloranilic acid cannot be accomplished in this way, as my many fruitless experiments with this end in view prove; and this is decidedly in favor of Fittig's formula. If we imagine in this formula the two hydrogen atoms to be absent, there is formed a compound which is just as incapable of existence as the radical methyl, since the valences set free at the carbon atoms containing chlorine cannot saturate one another. The compound,  , is not conceivable.

A diquinone, $C_6Cl_2O_4$, if it can be formed, must certainly be obtained by treating the dry silver salt of chloranilic acid with bromine according to the following equation:

$$C_6Cl_2O_4Ag_2 + Br_2 = C_6Cl_2O_4 + 2AgBr.$$

I carried out this experiment and treated silver chloranilate with one and two molecules bromine, but invariably obtained as sole product a compound which proved to be dibrom-dichlor-tetraketo-hexamethylene. This is the case even when less than one molecule of bromine is used; the only difference being that much silver chloranilate is left unchanged.

This reaction in the first place decides clearly in favor of Fittig's formula, and in the second place against the existence of a para bond; the reaction takes place as follows:

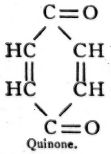


The hydroxyl groups in chloranilic acid can thus only be converted into quinone groups provided the valences set free at the two carbon atoms containing chlorine are correspondingly saturated. The valences cannot mutually paralyse one another, *i. e.* no union in the para position takes place; still less is it possible for these two carbon atoms to remain trivalent.

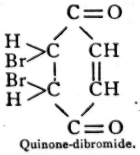
The behavior of the anilic acids is thus clearly in favor of Fittig's quinone formula, but the direct experimental proof that quinones have two doubly bound carbon atoms is yet wanting.

This it has been possible for me to furnish in a simple and most convincing manner in the case of quinone itself. This substance, namely, absorbs bromine with the same energy as ethylene itself without evolution of hydrobromic acid.

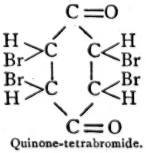
On adding one or two molecules of bromine to a solution of quinone in chloroform there is formed quinone dibromide and quinone tetrabromide.



Quinone.



Quinone-dibromide.

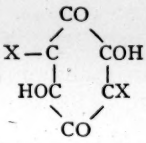


Quinone-tetrabromide.

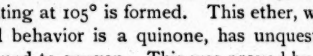
The proof that the addition products obtained have the above constitution is unquestionable, and the facts are thus so definitely and exclusively in favor of Fittig's formula that I regard a doubt concerning the constitution of benzoquinone as no longer admissible.

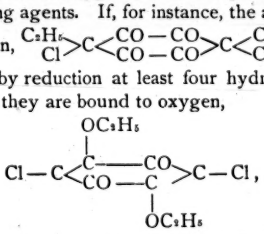
Experimental Part.

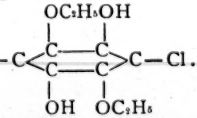
The anilic acids contain two hydroxyl groups,



In my first paper[1] on the anilic acids I described many fruitless experiments to obtain alkyl or acid ethers of nitranilic acid. The intention thereby was to prove whether in the ethers the substituted group is bound to carbon or to oxygen, and thus to draw further conclusions concerning the position of the hydrogen atoms in the anilic acids themselves.

Such ethers are, however, easily obtained from chloranilic acid by means of its silver salt. Stenhouse[2] found, namely, that of allowing silver chloranilate to stand with ethyl iodide, ethyl chloranilate melting at 105° is formed. This ether, which both in appearance and behavior is a quinone, has unquestionably the alkyl groups bound to oxygen. This was proved by its behavior towards reducing agents. If, for instance, the alkyl groups were bound to carbon,  , the substance must take up by reduction at least four hydrogen atoms; if on the other hand they are bound to oxygen,



only two hydrogen atoms can be added, forming ethyl hydrochloranilate,  .

On treating a hot alcoholic solution of ethyl chloranilate with zinc-dust and hydrochloric acid or with sulphurous acid, there is always formed ethyl dihydro-chloranilate, melting at 152°. This

[1] This Journal **11**, 17.

[2] Chem. Soc. Journal **23**, 4, and Ann. Chem. (Liebig), Suppl. **8**, 14.

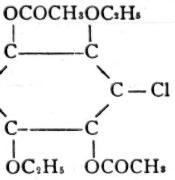
substance has since been described by Kehrmann.[1] The analysis of the compound dried at 110° gave the following result:

0.2128 gram substance gave 0.3485 gram CO_2 and 0.0908 gram H_2O.

	Theory for $C_6\begin{cases}(OH)_2\\(OC_2H_5)_2\\Cl_2\end{cases}$	Found.
C	44.94	44.67
H	4.49	4.74

As regards the properties, etc., of the substance I refer to the paper of Kehrmann.[1] Noteworthy concerning its behavior is the fact that the ether cannot be reduced further even after heating for six hours on a water-bath with sodium amalgam, as well as the fact that it can be boiled in alkaline solution if the air is excluded without the slightest change. Ethyl chloranilate, on the other hand, is saponified by simply adding dilute sodic hydrate to it. The ethers of oxyquinones thus are decidedly less stable than those of phenols, just as carboxylated and halogenated quinone derivatives are far more reactive than the corresponding genuine benzene derivatives.

Ethyl Diacetyl-hydrochloranilate,



On heating ethyl hydrochloranilate (melting point 152°) for about three hours with acetic anhydride it is converted quantitatively into a diacetyl derivative, which, as it is difficultly soluble in boiling alcohol, is easily obtained pure. Twice recrystallised from alcohol, it was obtained in colorless four-sided prisms melting at 172°.

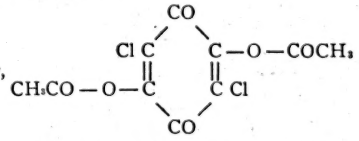
0.2198 gram substance dried at 110° gave 0.3826 gram CO_2 and 0.0911 gram H_2O.

[1] J. prakt. Chem. **40**, 373. In this connection I would like to state that Kehrmann, in his last papers (J. prakt. Chem. **39**, 318; **40**, 365), describes experiments the carrying out of which I had by full right of priority reserved for myself (Ber. d. chem. Gesell. **20**, 2027; this Journal **11**, 17). Especially is this the case with his recent publication on the replacement of the chlorine atoms in chloranil.

Theory for $C_6\begin{cases}(OCOCH_3)_2\\(OC_2H_5)_2\\Cl_2\end{cases}$.		Found.
C	47.87	47.48
H	4.56	4.60

The compound is volatile without decomposition, and in alcoholic solution by means of alkalies is instantly converted back into ethyl hydrochloranilate again.

Diacetyl-chloranilate,



The direct proof that the anilic acids possess two hydroxyl groups has not yet been furnished by the isolation of a diacetyl derivative. The reason for this lies in the fact that the acetyl derivatives of oxyquinones are still less stable than those of phenols.

The diacetyl derivative of chloranilic acid can be obtained in the following way: Silver chloranilate (which was always prepared by adding a cold solution of the sodium salt to a solution of 1½ times the calculated amount of silver nitrate and thereupon dried at 140°) is suspended in a small amount of ether (free from water and alcohol), and thereto twice the calculated amount of acetyl chloride, dissolved in ether, is added. The reaction is completed almost immediately, and in order to isolate the product formed the ether and excess of acetyl chloride is allowed to evaporate over sulphuric acid in a vacuum. The residue, after having been dried on clay plates, is extracted two to three times with warm, pure ether. After the ethereal solution has been concentrated by distilling off the ether in part, diacetyl chloranilate crystallises out in yellow needles, and the first portions separating out are perfectly pure; the later portions, however, are best crystallised from hot anhydrous benzene, from which, on cooling, the substance separates out in great part in the form of yellow needles.

0.2952 gram substance dried at 110° gave 0.4399 gram CO_2 and 0.0618 gram H_2O.

Theory for $C_6\begin{cases}O_2\\(OCOCH_3)_2\\Cl_2\end{cases}$.		Found.
C	40.95	40.67
H	2.05	2.36

The compound is volatile without decomposition, and melts at 182½°. Cold water has no effect on it, and boiling water converts it very slowly into chloranilic acid.

The substance is extremely unstable in alcoholic or acetic acid solution; it dissolves in alcohol at first with a yellow color, but even when only traces of water are present the solution, slowly on standing, instantly on heating, becomes colored violet. On adding water to the alcoholic solution, saponification to chloranilic acid and acetic acid takes place instantly. For recrystallising the diacetyl derivative, therefore, only such solvents can be used which contain no water and also do not absorb water.

The above facts, namely:

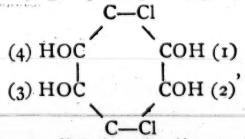
(1) That ethyl chloranilate takes up only two hydrogen atoms by reduction;

(2) That this substance is saponified by dilute sodium hydrate in the cold;

(3) That an acetyl derivative of chloranilic acid has been obtained,

prove that in the ethers of chloranilic acid the substituted group is bound to oxygen. The conclusion that the salts as well as the acid itself have an analogous constitution is justifiable; the latter therefore possesses two hydroxyl groups.

Remarkably enough, it is impossible to remove the hydrogen atoms from the two hydroxyl groups by oxidising agents, and this led me at first to the thought that perhaps the two pairs of hydroxyl groups in hydrochloranilic acid possessed different functions. It was therefore necessary to prove that it is indifferent which pair of hydroxyl groups, 1, 3 or 2, 4,

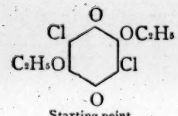


Hydrochloranilic acid.

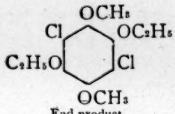
are converted by oxidation into the quinone group.

To decide this I proceeded as follows:

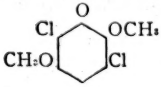
Chloranilic ethyl ether was reduced and the hydroquinone thus obtained converted into the methyl ether. In like manner chloranilic methyl ether was reduced and the hydroquinone obtained converted into the ethyl ether.



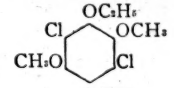
Starting point.
Chloranilic ethyl ether.



End product.
Methyl hydrochloranilic ethyl ether.



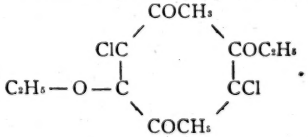
Starting point.
Chloranilic methyl ether.



End product.
Ethyl hydrochloranilic methyl ether.

If there were a difference of any kind between the pairs of hydroxyl groups the two end-products obtained must be isomeric; they were, however, found to be identical in every respect, and by oxidation with nitric acid both are converted into a mixture of ethyl and methyl chloranilate. Therefrom I draw the conclusion that the reason for the fact that the two remaining hydrogen atoms in hydrochloranilic acid cannot be removed by oxidation lies not in any difference between the pairs of oxygen groups in the para position, but that it is to be sought in the grouping of the carbon atoms forming the closed chain.

Dimethyl hydrochloranilic ethyl ether, or p-Dichlor-dimethoxy-diethoxy-benzene,



If ethyl hydrochloranilate be heated for one day in alcoholic solution with caustic potash and methyl iodide (1½ times the calculated amount) in a sealed tube at 100°, the two hydrogen atoms are replaced by methyl. After adding water, the product formed is extracted with chloroform and this solution washed with sodic hydrate and water. The chloroform solution, after having been dried with calcium chloride, is distilled off, and the residue recrystallised from dilute methyl alcohol. Thus colorless, long, flat needles were obtained, which melt at 103° and are volatile without decomposition. The yield was 1.5 gram from 2 grams hydroquinone taken.

I. 0.2286 gram substance, dried over sulphuric acid in a vacuum, gave 0.4070 gram CO_2 and 0.1130 gram H_2O.

II. 0.2109 gram substance gave 0.3742 gram CO_2 and 0.1104 gram H_2O.

III. 0.1336 gram substance gave 0.1304 gram AgCl (Carius).

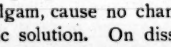
Theory for $C_8\begin{cases}(OCH_3)_2\\(OC_2H_5)_2\\Cl_2\end{cases}$.		Found.	
		I.	II.
C	48.81	48.55	48.39
H	5.40	5.51	5.89
Cl	24.07	24.15	

The substance is easily soluble in organic solvents. It can be boiled in alcoholic solution with sodic hydrate without change. Also reducing agents, as zinc dust and hydrochloric acid or sodium amalgam, cause no change even after long treatment in hot alcoholic solution. On dissolving the substance in fuming nitric acid, oxidation immediately takes place and water precipitates a yellow, flaky product which consists of a mixture of methyl and ethyl chloranilate. These can be separated by fractional crystallisation from methyl or ethyl alcohol, since the methyl ether is more difficultly soluble. The products obtained were in every respect identical with the corresponding ethers formed from silver chloranilate and methyl or ethyl iodide. Methyl chloranilate (melting point 142°) has recently been made in this way by Kehrmann.[1]

Finally, methyl chloranilate (made from the silver salt with methyl iodide) was converted into the hydroquinone,[2] melting point 196°, and this converted into the ethyl ether by heating for a day in a sealed tube at 100° with ethyl alcohol, caustic potash and ethyl iodide. The ethyl hydrochloranilic methyl ether thus obtained was in every respect identical with the above methyl hydrochloranilic ethyl ether melting at 103°.

Hexamethylene Derivatives from the Anilic Acids.

Dibrom-dichlor-tetra-keto-hexamethylene,



As already mentioned in the introduction, many experiments were carried out in order to remove the two hydrogen atoms in

[1] J. prakt. Chem. **40**, 370. [2] Ibid. **40**, 374.

chloranilic acid by oxidation, in order thus to obtain a diquinone $C_6Cl_2O_4$. In all the experiments with the most varied oxidising agents the substance was either left unchanged or entirely decomposed. In order finally to attain my object I attempted to remove the metal from the salts of the acid by means of bromine. The salt best adapted to this purpose is the silver salt, which was prepared as mentioned above under diacetyl chloranilic acid. It was suspended in pure anhydrous carbon bisulphide, and thereto was slowly added (care being taken to shake thoroughly) a dilute solution of bromine in carbon bisulphide solution. The reaction takes place instantly and is completed only after exactly two molecules of bromine have been added—a fact which in itself points to the conclusion that bromine has been taken up in the reaction product formed. Bromine acts in an analogous manner on the anhydrous sodium salt, but in this case the reaction takes place very slowly and is completed only after twenty-four hours.

The silver bromide is filtered off, and after distilling off a portion of the carbon bisulphide filtrate until crystals are seen at the sides of the flask, there separates out on cooling a large quantity of pale yellow, flat needles. These after being recrystallised once from carbon bisulphide were pure.

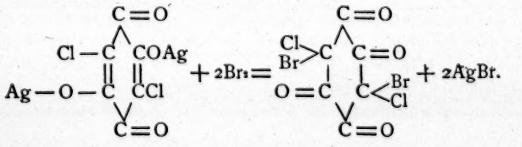
I. 0.3020 gram substance, dried over sulphuric acid in a vacuum, gave 0.2165 gram CO_2 and 0.0131 gram H_2O.

II. 0.3116 gram substance gave 0.2220 gram CO_2 and 0.0081 gram H_2O.

III. 0.2095 gram substance gave 0.3760 gram AgCl, AgBr, instead of 0.3784 gram AgCl, AgBr calculated.

	Theory for $C_4Br_2Cl_2O_4$.	Found. I.	II.
C	19.62	19.53	19.43
H	0.00	0.48	0.29
Br, Cl	62.91	62.54	...

Dichlor-dibrom-tetra-keto-hexamethylene has therefore been formed according to the following reaction:



A small quantity of the substance heated quickly in a test-tube melts sharply and then sublimes in flat needles or in cubes. Heated slowly in a capillary tube it begins to soften and decompose at 110°, and finally melts completely at 160°, decomposing with marked evolution of gas. It has a piercing odor.

Crystallised from carbon disulphide, in which it dissolves with pale yellow color and green fluorescence, the substance is obtained in long, flat, pale yellow needles, in six-sided plates or in cubic-like forms. The crystals are very hygroscopic and therefore lose their luster very quickly in the air, so that a goniometric measurement is not possible. The substance crystallises also very well from ether (free from alcohol and water), but it seems slowly (in 24 hours) to decompose the ether, since much hydrobromic acid is set free. A carbon disulphide solution of the tetra-keto derivative can be heated for a long time at 100° with molecular silver without change, and even when heated for two hours at 150° it was only very slightly decomposed.

On treating an ethereal solution with phenylhydrazine there is formed a yellow, flaky precipitate, which can be obtained in colorless pearly scales by recrystallisation from acetic acid. The product, however, is not a hydrazone, but an unstable addition product (various analyses gave figures from which it is impossible to deduce a formula), which is immediately decomposed by water with liberation of phenylhydrazine. It was also impossible to obtain with *o*-toluylene-diamine a quinoxaline derivative, although a dirty dark-brown precipitate results on adding this reagent to an ethereal solution of the tetra-keto compound. In the absence of water, therefore, the compound is tolerably stable, but if water be present it is very quickly decomposed. On pouring a small amount of water over the solid substance, marked evolution of heat and of carbonic anhydride are noticeable. The substance dissolves in much water, with yellow color and green fluorescence, and then slowly evolution of carbonic anhydride takes place.

When the decomposition is completed, ether extracts from the aqueous solution no longer the hexamethylene derivative, but a yellowish oil, which is an acid and forms an ammonium salt that crystallises well. The same oil is formed directly from chloranilic acid salts (sodium or potassium salt), if these in solution be treated with two molecules of bromine water. The hexamethylene derivative, which must be formed as the intermediate product,

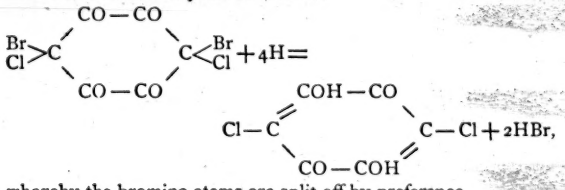
can thus in fact not be isolated at all by this method. This reaction, whereby penta-methylene derivatives are formed, will be explained later. The penta-methylene compounds here formed, of which two possibly may be present, were not investigated further.

Dichlor-dibrom-tetra-keto-hexamethylene is very easily converted back into chloranilic acid by means of sulphurous acid. The substance is best added in small portions to an aqueous solution of sulphurous acid, whereby chloranilic acid immediately separates out completely. The reduction never takes place quantitatively, since a partial conversion into the penta-methylene derivative cannot be prevented. From 1 gram substance in the most favorable case, 0.2 gram chloranilic acid containing water of crystallisation was obtained.

A halogen determination proved that the substance was pure chloranilic acid, containing not a trace of bromanilic acid.

0.1136 gram substance dried at 130° gave 0.1550 gram AgCl; calculated, 0.1560 gram AgCl. Therefrom (0.1550 gram AgCl) was obtained by heating in an atmosphere of hydrogen 0.1159 gram Ag, instead of 0.1166 gram Ag, calculated for AgCl.

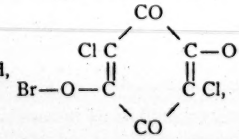
The reaction takes place as follows:



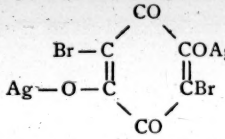
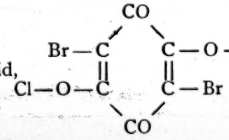
whereby the bromine atoms are split off by preference.

That the substance possesses the constitution

and is not an ether of hypobromous acid,



, is proved even by the comparatively great stability of the substance in the absence of water; furthermore, such an ether must undoubtedly give with water chloranilic acid.

A further proof for the constitution of the substance as given above is the following: The *same substance*, dichlor-dibrom-tetra-keto-hexamethylene, is formed by the action of chlorine on silver bromanilate,  . In this case, were the compound not a hexamethylene derivative, an ether of hypochlorous acid,  , would have been formed, and this must unquestionably be readily converted into bromanilic acid.

Since the two products, however, are identical, a new proof is won for the constitution of the substance as given.

The observation that the compound under discussion gives pure chloranilic acid by reduction with sulphurous acid is noteworthy. The chlorine atoms must, therefore, be more firmly bound to carbon than the bromine atoms. In favor of this explanation is the fact that tetrachlor-tetraketo-hexamethylene, obtained from silver chloranilate with chlorine, is *not* converted back into chloranilic acid by means of sulphurous acid.

Tetra-brom-tetra-keto-hexamethylene,

$$Br_2=C<\begin{matrix}CO-CO\\CO-CO\end{matrix}>C=Br_2.$$

This substance was obtained from silver bromanilate by means of bromine, and the preparation and purification is exactly the same as with the above dibrom-dichlor derivative. It crystallises in pale yellow flat needles, which, analysed, gave the following result:

0.2467 gram substance, dried over sulphuric acid in a vacuum, gave 0.1430 gram CO_2 and 0.0105 gram H_2O.

0.1636 gram substance gave 0.2678 gram AgBr (Carius).

	Theory for $C_6Br_4O_4$.	Found.
C	15.79	15.81
H	0.00	0.47
Br	70.18	69.54

When heated slowly the substance shows exactly the same behavior as dibrom-dichlor-tetra-keto-hexamethylene; heated quickly it cannot, however, be sublimed without decomposition as is the case with the latter. It has a sharp piercing odor.

Sulphurous acid naturally converts the compound back again into bromanilic acid; the behavior of the substance towards water must be discussed at some length.

On pouring a small amount of water over the solid substance a violent reaction, accompanied by marked evolution of heat and of carbonic anhydride, takes place, just as is the case when a mineral acid is added to a carbonate.

The aqueous solution now contains an acid, namely tribrom-oxy-diketo-pentamethylene, $Br_2{=}C\begin{smallmatrix}COH\\ \diagup\quad\diagdown\\ C\text{—}C\\ O\quad O\end{smallmatrix}CBr.$

In order to isolate it, the solution is acidified with sulphuric acid and repeatedly extracted with ether. The product obtained after evaporating the ether was purified according to the directions given by Hantzsch[1] (who obtained it from potassic bromanilate by means of bromine in caustic potash solution), namely, through the ammonium salt. It was then completely analysed.

0.2966 gram substance, dried over sulphuric acid in a vacuum, gave 0.1853 gram CO_2 and 0.0152 gram H_2O.

0.1168 gram substance gave 0.1886 gram AgBr (Carius).

	Theory for $C_5HO_3Br_3$.	Found.
C	17.19	17.02
H	0.29	0.57
Br	68.70	68.70

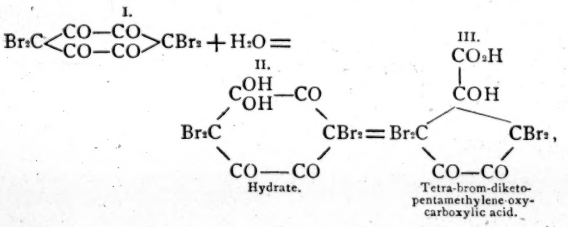
Since the substance is a monobasic acid, it is better to regard it as tribrom-oxy-diketo-pentamethylene and not as tribrom-triketo-pentamethylene, as Hantzsch assumes.

An experiment to determine the amount of carbonic anhydride given off in the formation of this substance proved that one molecule is split off.

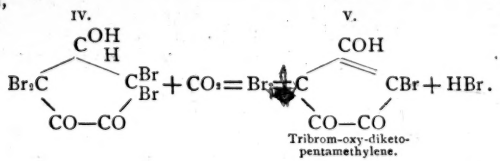
[1] Ber. d. chem. Ges. 21, 2440.

1.6728 gram substance (tetrabrom-tetraketo derivative) gave, when treated in a flask with a small amount (30–50 cc.) of water after expelling the carbonic anhydride formed with air, 0.1460 gram CO_2 instead of 0.1614 gram calculated. A small loss of carbonic anhydride was unquestioned, since the experiment was not carried out with all possible precautions.

The reaction probably takes place as follows:



which spontaneously loses carbonic anhydride and hydrobromic acid,



The explanation of the mechanism of the reaction as given is based upon Zincke's[1] experiments with β-naphtho-quinone, where, by means of alkalies, the conversion of the ortho-diketone group into the oxy-carboxyl group takes place; it is justifiable as well in this case since we have to do with a diortho-diketone, but the intermediate products II–IV are here not capable of existence.

Remarkable is the fact that the conversion into the penta-methylene derivative is here caused almost instantly by *pure water*. This proves better than any fact yet known the great tension existing in the hexamethylene ring and the tendency to go over into the stable pentamethylene ring. The "tension theory" of v. Baeyer[2] receives thereby a new very convincing experimental proof.

[1] Ber. d. deutsch. chem. Gesell. **19**, 2500; **20**, 1165. [2] Ibid. **18**, 2277.

Tribrom-oxy-diketo-pentamethylene is also formed quantitatively by treating an aqueous solution of potassium or sodium bromanilate with two molecules of bromine water.

It is a well known fact that the anilic acids, as well as their salts,[1] are converted by means of oxidising agents, especially by means of halogens in the presence of water, into fatty compounds or pentamethylene derivatives. The mechanism of these reactions has heretofore not been understood, for the reason that the first intermediate products formed, namely, the tetra-keto-hexamethylene derivatives, were not isolated, since the oxidation was carried out in aqueous solution, in which, as we now know, they are instantly decomposed.

Thus Hantzsch describes in his first paper,[2] "Ueber Spaltungsprodukte der Chlor- und Bromanilsäure," a substance which he calls bromanilic acid bromide, and later,[3] by reason of my paper in this Journal, Vol. **11**, p. 26, he considers it to be tetra-brom-tetra-keto-hexamethylene. It is, however, impossible that this chemist could have obtained this compound by his method of preparing the substance, since the tetrabrom derivative is, as I have shown, almost instantly decomposed by water, and, furthermore, possesses entirely different properties from those shown by Hantzsch's product. I have therefore repeated his experiments and think that the product first described as bromanilic acid bromide was nothing but tribrom-oxy-diketo-pentamethylene, which contains at first an equal amount of bromanilic acid, and after its purification must have still contained traces of bromanilic acid. The melting point (184°–186°), as well as the analysis (percentage of bromine found = 69; percentage calculated = 68.8), agrees well for the pentamethylene derivative, which, when perfectly pure, melts at 191°.

On treating silver chloranilate, suspended in pure carbon bisulphide, with *dry* chlorine until about three-fourths of the silver salt has been changed into silver chloride, tetra-chlor-tetra-keto-hexamethylene was obtained, after concentrating the carbon bisulphide filtrate, in the form of pale yellow needles fully a centimeter in length. The substance is volatile without decomposition and sublimes in yellow needles which have a piercing odor. It is,

[1] Hantzsch: Ber. d. chem. Gesell. **21**, 2439; **22**, 2841; Hantzsch and Zeckendorff: Ber. d. chem. Gesell. **20**, 1308; Levy and Jedlicka: Ann. Chem. (Liebig) **249**, 66; Nef, this Journal **11**, 17.

[2] Ber. d. chem. Gesell. **21**, 2439. [3] Ibid. **22**, 2845.

however, so very hygroscopic that it deliquesces in a very short time in the air, and even when kept in a desiccator it slowly decomposes. I regarded an analysis of it as superfluous, and in any case it would be very difficult to carry out.

Tetra-chlor-tetra-keto-hexamethylene, $Cl_2C<\begin{matrix}CO-CO\\CO-CO\end{matrix}>CCl_2$, behaves towards water exactly as the corresponding tetra-bromine derivative, and thus trichlor-oxy-diketo-pentamethylene, $Cl_2C<\begin{matrix}COH\\CO-CO\end{matrix}>C-Cl$, was obtained. As regards its properties, as well as those of the ammonium salt, I can confirm the statements of Hantzsch,[1] who obtained it in a different way. As already mentioned, tetra-chlor-tetra-keto-hexamethylene differs from the corresponding tetrabrom- and dibrom-dichlor derivative in its behavior towards sulphurous acid, which in this case does not convert it into chloranilic acid. This is due to the fact that the chlorine atoms are bound more firmly to carbon, and therefore the fact that dibrom-dichlor-tetra-keto-hexamethylene gives by reduction with sulphurous acid pure chloranilic acid, is now no longer surprising.

The conversion of the tetrachlor derivative into hydrochloranilic acid is, however, possible if more powerful reducing agents be taken, as zinc dust and acetic acid.

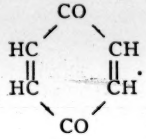
From the explanation given above of the conversion of the tetra-keto-hexamethylene into pentamethylene derivatives, it follows that tetra-chlor-diketo-pentamethylene-oxycarboxylic acid, which in all probability must have been formed as an intermediate product (III), is not capable of existence.

Now, Hantzsch[2] describes this compound as an especially stable product, and I therefore believe that the substances which this chemist has obtained by the action of hypochlorous acid salts on chloranilic acid, must possess a different constitution from that at present given to them.

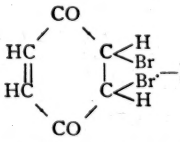
Finally, I would state that this investigation also confutes the assumption of the existence of tautomerism in the anilic acid series. The experiments prove that the metal in the anilic acid salts is bound to oxygen, and the hydroxyl formula suffices to explain fully and simply all the reactions shown by these acids.

[1] Ber. d. chem. Gesell. **21**, 2435. [2] Ibid. **22**, 2846.

BENZOQUINONE contains two doubly bound carbon atoms,



Quinone-dibromide,



—If quinone be dissolved in dry chloroform and a 5 per cent. solution of bromine in chloroform be added, all the bromine is instantly absorbed without the slightest evolution of hydrobromic acid. After one molecule of bromine has been added the yellow solution is allowed to evaporate spontaneously, and a substance possessing a high specific gravity and crystallising in flat needles is obtained, which after pulverising and washing with little alcohol is obtained pure. It melts at 86° and can also be purified by dissolving in chloroform and precipitating with petroleum ether (boiling point 40°–50°). This substance has long been known (since 1881), but because of its peculiar behavior Sarauw,[1] who discovered it, regarded it as an isomeric dibrom-hydroquinone, as

$$C_6H_3Br\begin{cases}OBr\\OH\end{cases}, \text{ or as } C_6H_3BrO_2+HBr.$$

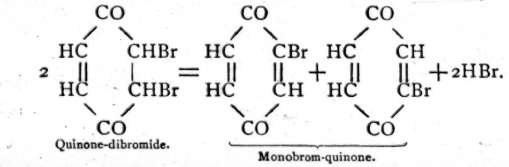
Hereby is again appended the analysis of Sarauw:

Theory for $C_6H_4O_2, Br_2$.		Found.
C	26.86	26.89
H	1.41	1.66
Br	59.70	60.03

As regards its properties I can confirm the statements of Sarauw; the substance, which has a pale yellow color, possesses, however, a distinct greenish tint, since the solutions also are colored greenish yellow, and it also has a distinct but faint odor of quinone. The following concerning its behavior is noteworthy: The substance dissolves easily, in the cold, in fuming nitric acid, and can be precipitated again unchanged by the addition of water

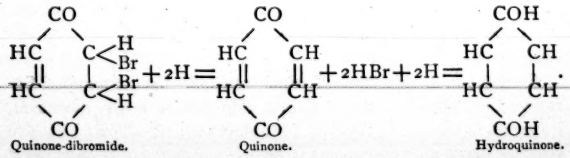
[1] Ann. Chem. (Liebig) **209**, 111.

even after boiling with nitric acid. It is insoluble in cold water; on boiling with water hydrobromic acid is slowly and quantitatively split off, and, on cooling, monobrom-quinone[1] (melting point 56°) crystallises out. The same reaction takes place on heating the substance in solution as was proved in the case of an alcoholic and an acetic acid solution.



Hydrobromic acid is evolved when the solid substance is heated very slightly above its melting point. If the temperature be low and the substance heated carefully, monobrom-quinone is formed; at a higher temperature much *p*-dibrom-hydroquinone[2] (melting point 186°) is formed. The monobrom-quinone thus formed at first oxidises the hydrobromic acid, forming monobrom-hydroquinone, which is then instantly converted by the bromine set free into *p*-dibrom-hydroquinone (*vide* Sarauw: Liebig's Annalen **209**, 108).

All these reactions *seem* to point to the fact that in quinone-dibromide one bromine atom is more firmly bound than the other. This, however, is not the case. If quinone-dibromide be dissolved in acetic acid and zinc dust be added, and finally the solution be heated gently, there is formed quantitatively pure hydroquinone (melting point 169°).



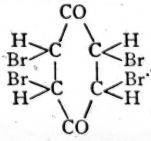
The two bromine atoms added in the ortho position are thus removed and the double bond again restored, just as v. Baeyer[3]

[1] Sarauw; Ann. Chem. (Liebig) **209**, 106. [2] Ibid. **209**, 109.
[3] Ann. Chem. (Liebig) **245**, 103; **251**, 261.

found to be the case with his ortho-dibrom addition-products of hydrogenated terephthalic acids.

Quinone-dibromide is decomposed by sodic hydrate with marked evolution of heat and deep brown coloration; on adding an acid to the solution obtained a brown flaky substance is precipitated. Very noteworthy is the above mentioned stability towards fuming nitric acid, a fact which is also so noteworthy in the cases of quinones themselves.

Quinone-tetrabromide,



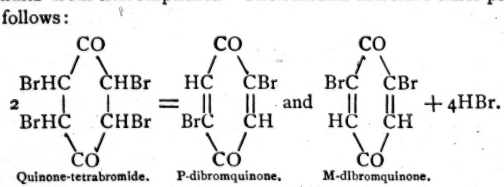
—On adding to a chloroform solution of quinone two molecules of bromine (5 per cent. solution in chloroform), or to a chloroform solution of quinone-dibromide one molecule of bromine, decoloration sets in at first almost immediately, but finally very slowly, and there soon separates out a colorless product in the form of very heavy scales. If the bromine solution contains some hydrobromic acid the absorption of the bromine is immediate, as well as also the separation of the colorless product. In the absence of hydrobromic acid it is several hours before complete absorption of bromine takes place, but very soon (in about 20 minutes) quinone-tetrabromide begins to crystallise out in colorless pearly scales. These can be filtered off directly without waiting for the total absorption of the bromine, and, after washing repeatedly with cold chloroform, they are perfectly pure. In the preparation as given above, at first not the slightest trace of hydrobromic acid is noticeable, and only towards the end are small quantities apparent. The yield of tetrabromide is 4.5–5 grams from 3 grams quinone (calculated 11.9 grams). Thus, while in the case of the dibromide the yield is almost quantitative, in this case secondary reactions also take place. The analysis of the substance washed repeatedly with chloroform gave the following result:

0.4976 gram substance, dried over sulphuric acid in a vacuum, gave 0.3058 gram CO_2 and 0.0486 gram H_2O.

0.2008 gram substance gave 0.3498 gram AgBr (Carius).

	Theory for $C_6H_4O_2Br_4$.	Found.
C	16.82	16.76
H	0.93	1.08
Br	74.77	74.12

The substance is very difficultly soluble in the cold in all solvents; on heating in solution, hydrobromic acid is split off. The solid substance decomposes also in the same way if kept for a time in closed vessels. In attempting to determine the melting point a yellow coloration becomes noticeable at 110°, which constantly becomes more intense until finally the substance melts between 170°–175° with marked evolution of hydrobromic acid. Two molecules of hydrobromic acid can be split off quantitatively as follows: quinone-tetrabromide is suspended in alcohol containing about 10–15 per cent. water, and the solution heated to the boiling point; the tetrabromide dissolves slowly with yellow coloration, and on addition of water a yellow product is precipitated, which is a mixture of about equal parts of meta- and para-dibromquinone. The separation of these isomers could readily be accomplished, since para-dibromquinone is much more difficultly soluble in ether than the meta compound. Thus the para derivative,[1] melting at 188°, was obtained, and for further identification it was converted into the hydroquinone[2] (melting point 187°). The meta-dibromquinone obtained (melting point 122°) was found to be identical with the product obtained by Levy and Schultz[3] from tribromphenol. The reaction therefore takes place as follows:



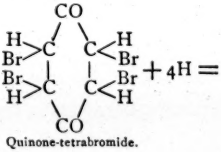
Quinone-tetrabromide. P-dibromquinone. M-dibromquinone.

Quinone-tetrabromide thus exactly as the dibromide has a great tendency to split off hydrobromic acid. The above reaction also takes place on heating the solid substance directly; in this case, however, it is necessary to heat very carefully (not higher than 120°), otherwise the isomeric dibromquinones first formed act on the hydrobromic acid and tri- and tetra-bromhydroquinone result. If, for instance, quinone-tetrabromide be heated to its melting point hydrobromic acid is given off rapidly, and at the same time a small amount of bromine is set free. The residue now consists

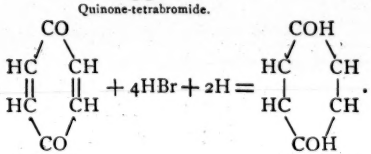
[1] Sarauw: Ann. Chem. (Liebig) **209**, 113. [2] Ann. Chem. (Liebig) **209**, 109.
[3] Ann. Chem. (Liebig) **210**, 159.

in great part of tribromhydroquinone with some tetrabromhydroquinone. The formation of these substances is easily explained when one considers that dibromquinone is converted by hydrobromic acid into tribrom- and tetrabromhydroquinone.[1]

These facts *seem* again to point to the conclusion that in quinone-tetrabromide two bromine atoms are more firmly bound than the other two. This is, however, only apparent. On treating quinone-tetrabromide with zinc dust and acetic acid there is formed quantitatively pure hydroquinone, melting point 169°, according to the equation:



Quinone-tetrabromide.



Quinone. Hydroquinone.

The pairs of bromine atoms added in the ortho position are thus removed just as in the case of quinone-dibromide, and the double bonds again restored. Sodic hydrate decomposes quinone-tetrabromide with marked evolution of heat and deep brown coloration. The tetrabromide also resembles the dibromide in its behavior towards fuming nitric acid, in which it is insoluble in the cold, but on warming it dissolves in very small amount, and on cooling it crystallises out again unchanged in colorless scales.

The above facts prove unquestionably that quinone adds two and four atoms of bromine, forming addition products which show a remarkable but now readily comprehensible behavior. Quinone is *yellow*, and has a *strong smell;* quinone-dibromide, *pale yellow* with a greenish tint and *faint odor;* quinone-tetrabromide, which is nothing but tetrabrom-*p*-diketo-hexamethylene, is *colorless* and *inodorous*, just as *p*-diketohexamethylene itself.[2]

[1] Sarauw: Ann. Chem. (Liebig) **209**, 117.

[2] Herrman: Ann. Chem. (Liebig) **211**, 332; v. Baeyer and Noyes; Ber. d. chem. Ges. **22**, 2168.

The experiments with quinone-di- and tetrabromide, as well as experiments to convert nitranilic acid and quinone-dioxyterephthalic ether into hexamethylene and pentamethylene derivatives, according to the method discovered above, will be continued.

In these experiments I have again been most zealously assisted by Dr. V. Paepcke, to whom I here express my warmest thanks.

WORCESTER, MASS., *May* 30, 1890.

ON THE ACTION OF METALLIC CADMIUM ON THE HALOGEN SALTS OF CADMIUM, AND ON THE SUB-HYDROXIDE AND SUB-OXIDE OF CADMIUM.

BY H. N. MORSE AND H. C. JONES.

If anhydrous chloride of cadmium is heated with metallic cadmium, in a vacuum or in an atmosphere of nitrogen, to the fusing point of the chloride, the molten salt quickly assumes a fine garnet red color. In order to investigate this phenomenon we prepared a quantity of the chloride by dissolving the redistilled metal in hydrochloric acid, evaporating to dryness with an excess of the acid, and distilling the residue in a current of dry hydrochloric acid gas. For the purpose of distillation, a long platinum boat containing the chloride was placed in a combustion tube and heated in a current of the acid gas until the material had disappeared from the boat and collected upon the bottom of the glass tube. The chloride, thus freed from water and oxychloride, and an excess of metal were placed in a long-necked flask of hard glass, and, after displacement of the air by nitrogen, heated to the melting point of the chloride. The liquid chloride attained its maximum depth of color within a few minutes, nevertheless the heating was continued for five hours. It was observed that globules of metal collected upon the sides of the flask whenever the temperature was allowed to rise much above that required for the fusion of the chloride. For this reason no more heat was applied than was necessary to keep the contents of the flask in a liquid condition. During the cooling the flask was gently jarred in

order to facilitate the sinking of any metal which might be retained by the chloride.

The solidified material had a grayish white color, and a cleavage resembling that of talc or brucite. Under the microscope it appeared to be homogeneous and free from metal. It also gave no metallic streak when rubbed between agate surfaces. An analysis gave:

Cadmium.	Chlorine.
64.27 per cent.	35.61 per cent.

These proportions are nearly those of a compound having the composition Cd_4Cl_1, in which the calculated percentages are:

Cadmium.	Chlorine.
64.34	35.65

In order to determine whether this close approximation to definite atomic proportions might not be accidental, we reheated the material with an excess of the metal for twenty hours. An analysis of the product gave:

Cadmium.	Chlorine.
64.33 per cent.	35.75 per cent.

Two other portions of the substance were then prepared from fresh materials. On analysis, the first gave:

Cadmium.	Chlorine.
64.30 per cent.	35.61 per cent.
64.35	35.66

the second:

Cadmium.	Chlorine.
64.42 per cent.	35.74 per cent.

When the new substance is heated it fuses to a red liquid, and then breaks up into metal and the chloride of cadmium. Its reactions are, in general, those of a strong reducing agent. Treated with nitric acid it yields oxides of nitrogen. With dilute hydrochloric, sulphuric and acetic acids it gives free hydrogen. In the presence of dilute acids it reduces mercuric to mercurous chloride or to metallic mercury.

Three determinations of its reducing power were made, with portions of different preparations, by dissolving in hydrochloric acid and exploding the hydrogen which was evolved with air. The following results were obtained:

Hydrogen found.	Hydrogen calculated for Cd_4Cl_7.
15.67 cc.	15.65 cc.
11.80	11.82
23.00	23.03

Notwithstanding the fact that the cadmium and chlorine are present in atomic proportions which remain constant however long the chloride is heated with an excess of the metal, and the fact that the material appears to be homogeneous, it is by no means clear that the substance is a definite chemical compound. It appears to us quite as probable that, in the molten condition, it is a solution of a cadmous chloride in the ordinary chloride of cadmium, or possibly a double compound of the two; and that the cadmous compound cannot accumulate beyond a certain limit, owing to the ease with which it breaks up into metal and the original chloride. This view as to its composition is somewhat strengthened by the fact that when the substance is treated with water it yields the chloride and a cadmous hydroxide of normal composition, CdOH.

The anhydrous bromide of cadmium was prepared by dissolving the carbonate in aqueous hydrobromic acid, evaporating to dryness with an excess of the acid, and heating the residue in a current of dry hydrobromic acid gas. When the bromide was heated with the metal in an atmosphere of nitrogen, it behaved in all respects like the chloride under the same conditions. The fused material quickly assumed a deep red color. On being more highly heated it gave up metal which collected in globules or in a thin film upon the sides of the flask. On cooling it solidified to a grayish white mass which resembled in crystalline structure the product which was obtained by a similar treatment of the chloride. This, also, appeared to be free from metal, and homogeneous. The substance was found to contain cadmium and bromine in the proportions represented by the formula Cd_4Br_7. Two analyses gave:

Cadmium.	Bromine.
44.59 per cent.	55.46 per cent.
44.57	55.47

The calculated percentages for Cd_4Br_7 are:

Cadmium.	Bromine.
44.45	55.55

As in the case of the chloride, it was found that reheating with the metal did not appreciably change the proportions of the constituents.

The substance is a strong reducing agent: giving with nitric acid, oxides of nitrogen; with dilute hydrochloric, sulphuric or acetic acid, free hydrogen; and with mercuric chloride, mercurous chloride or metallic mercury. Treated with water, it yielded the bromide of cadmium and cadmous hydroxide, CdOH.

The iodide of cadmium was prepared in the same manner as the bromide. Heated with the metal in an atmosphere of nitrogen, it acquired a deep red color. On cooling, the solidified material presented an appearance like that of the products obtained from the chloride and bromide. Owing to the high specific gravity of the iodine compound, some difficulty was experienced in obtaining a preparation free from metal. But this difficulty was finally overcome by keeping the material for a long time just above its melting temperature and constantly jarring the flask. Two determinations of cadmium in the first satisfactory preparation gave 31.43 and 31.51 per cent. of the metal. As these results did not correspond to a composition represented by the formula Cd_4I_7, which our experience with the chloride and bromide had led us to expect, we reheated the material for several hours with the metal. But two analyses of the last product gave:

Cadmium.	Iodine.
31.44 per cent.	68.65 per cent.
31.39	68.68

showing that the iodide had absorbed during the first heating all of the metal which it was capable of retaining. The analytical results suggest the formula $Cd_{12}I_{23}$ or $CdI + 11CdI_2$, in which the calculated percentages are:

Cadmium.	Iodine.
31.53	68.47

In its conduct towards dilute hydrochloric and acetic acids and water, the substance behaves like the products obtained from the chloride and bromide.

When the substances just described are treated with water they yield the ordinary halogen salts of cadmium which dissolve; a small quantity of hydroxide which renders the water turbid;

and heavy, transparent, highly lustrous, crystalline substances, which quickly lose their crystalline appearance and pass over into a grayish white amorphous compound, which we have found to be normal cadmous hydroxide, CdOH. All attempts to determine the composition of these intermediate crystalline compounds have failed, owing to the rapidity with which, in the presence of water, they are converted into hydroxide. Even with the most rapid work they could not be isolated in an undecomposed condition.

Analyses of the partially decomposed materials gave quite variable proportions of metal and halogen, but never less than eight equivalents of the former to one of the latter. The production of cadmic hydroxide is evidently an essential part of the decomposition by water; since the substances, before the treatment with water, were free from oxygen, as we assured ourselves by repeated analyses. But we are not able, as yet, to explain its origin.

Notwithstanding the rapidity with which the decomposition of the crystalline compounds begins, long continued washing is necessary in order completely to remove the halogen. The extraction of the last traces of chlorine, bromine or iodine is hastened by the use of warm instead of cold water. But the temperature must not exceed 50° C. In water whose temperature approaches the boiling point, the hydroxide is slowly decomposed with separation of metal.

The new hydroxide is a strong reducing agent. It dissolves in dilute acids; yielding with nitric acid oxides of nitrogen, with other acids free hydrogen. The material which was examined more particularly by us was derived from the chloride. After washing with slightly warmed water until the last traces of chlorine had disappeared, it was dried over phosphorus pentoxide and analyzed. The results were:

Cadmium.	Water.
86.93 per cent.	7.06 per cent.
86.91	

The calculated percentages for CdOH are:

Cadmium.	Water.
86.80	7.00

The determination of the water was made by placing a small tube containing the material in a larger and longer one and

heating in a bath of sulphuric acid. During the heating a slow current of dry nitrogen was passed over the substance.

When the temperature at which the sulphuric acid gives off dense white clouds is reached, the hydroxide gives up all of its water and passes over into a heavy yellow powder. Under the microscope this powder was found to consist of minute translucent crystals. Analyses of two specimens gave 93.14 and 93.17 per cent. of cadmium. The calculated percentage of metal in Cd_2O is 93.33. If water of too high temperature is employed in washing the hydroxide, the suboxide has a greenish tint, and the presence of free metal in it may be detected under the microscope and by rubbing between agate surfaces. If the yellow suboxide is strongly heated it breaks up into a mixture of oxide and metal which possesses a distinctly green color. A supposed suboxide of cadmium has been described by R. Marchand[1] as a green substance which can be obtained by heating the oxalate to the temperature of melting lead. But the product of such a decomposition of the oxalate was found by Vogel[2] to consist of a mixture of oxide and metal.

Towards acids the suboxide conducts itself like the subhydroxide.

It is a fact of some interest in connection with the periodic arrangement of the elements, that the tendency toward the formation of a lower series of compounds, which becomes so strongly developed in mercury, begins to exhibit itself in some slight degree in cadmium.

ON SILVER FORMANILIDE.

By W. J. Comstock and Felix Kleeberg.

That acid anilides can form salts with metals was first shown by Hofmann[3] in 1865, when he succeeded in preparing the sodium salt of formanilide. Salts of acid amides with the heavy metals had been prepared previously, and since that time numerous investigators have had occasion to work with similar compounds.

[1] Pogg. Ann. **38**, 143. [2] Jahresbericht 1855, 390. [3] Berl. Akad. Ber. 1865, 659.

Bunge[1] first prepared sodium acetanilide by acting with metallic sodium on the hot solution of acetanilide in xylene, and in the same paper states that he was unable to prepare silver salts of either form, or acetanilide. Hepp's well known synthesis of mono-methyl-aniline from sodium acetanilide shows that the structure of this salt is $C_6H_5N<^{Na}_{COCH_3}$.

Although Tobias[2] was unable to obtain methyl-formanilide from sodium formanilide, it has since been shown by Norton and Livermore,[3] as well as by Pictet and Crépieux,[4] that this synthesis is possible, so that in this latter salt as well sodium is united with the nitrogen. In the group of analogous thio-anilides, which differ from the ordinary acid anilides in that they are readily soluble in cold dilute alkalies, another structure must be assumed for the sodium salts. Wallach[5] showed that the sodium salt of thiacetanilide does not give the normal ethyl-thiacetanilide, $C_6H_5N<^{C_2H_5}_{CSCH_3}$ by treatment with ethyl bromide, but that an isomeric compound, $C_6H_5N=C<^{SC_2H_5}_{CH_3}$, which he called ethyl-iso-thiacetanilide, is formed. Since then the investigation of similar thio-anilides has led to the conclusion that in the sodium salts of bodies of this class, the metal is united with sulphur rather than with nitrogen.

Notwithstanding the failure of Bunge to obtain a silver salt of formanilide, it can be prepared in quantity with no more inconvenience than attends the preparation of other amorphous silver salts that are sensitive to light.

An investigation of this salt has led us to the interesting result that, although in sodium formanilide the metal is, as mentioned above, united with nitrogen, to the silver salt must be assigned the structure $C_6H_5N:C<^{OAg}_{H}$. If silver formanilide and methyl iodide are allowed to react in molecular proportions, silver iodide is formed together with a compound, the analysis of which gave results agreeing with formyl-mono-methyl-aniline, but whose properties and decompositions are entirely different. The boiling point and the characteristic odor show at once that the body is

[1] Ann. Chem. (Liebig), Suppl. **7**, 122. [2] Ber. d. chem. Gesell. **15**, 2452.
[3] Ibid. **20**, 2273. [4] Ibid. **21**, 1106. [5] Ibid. **11**, 1590.

not formyl-mono-methyl-aniline. With aniline the new compound reacts according to the equation

$$C_8H_9NO + C_6H_5NH_2 = C_{13}H_{12}N_2 + CH_3OH,$$

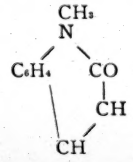
and the compound, $C_{13}H_{12}N_2$, is the well known diphenyl-formamidine, $CH\begin{matrix}\diagup NHC_6H_5 \\ =NC_6H_5\end{matrix}$, the structure of which can be regarded as settled. This reaction and the formation of the new compound from silver formanilide show beyond doubt that its structure is $C_6H_5N=C\begin{matrix}\diagup OCH_3 \\ \diagdown H\end{matrix}$; we shall speak of it hereafter as methyl-iso-formanilide, in conformity with the nomenclature adopted by Wallach for the corresponding thio-compounds, or as phenyl-form-imido-methyl ether, on account of its analogy to the imido ethers of Pinner. Below are given the details of the reaction. It is our intention to give a more complete study of this class of compounds at a future date, the object of this paper being to call attention to the behavior of silver formanilide, and the connection of our results with the question of the constitution of compounds containing the group $\begin{matrix}NH-CO \\ | \quad\ | \end{matrix}$, or $\begin{matrix}N=C.OH \\ | \quad\ | \end{matrix}$.

Compounds of this nature received a great deal of attention during the few years succeeding the publication by Baeyer and Oekonomedes[1] of their work on isatine. Essentially the same question had previously come up regarding cyanic and cyanuric acids, and the method of attacking the problem was the same, *i. e.* to study the ethers. If the ether contained the alkyl group attached to oxygen, it was regarded as proof that the original compound contained the group $\begin{matrix}N=C.OH \\ | \quad\ | \end{matrix}$, while the other arrangement of atoms (now frequently spoken of as the tautomeric form) was assumed when the ether contained the alkyl attached to nitrogen. This led to the adoption of formulæ containing the two different groups for compounds in which the same arrangement might well have been expected. For example, isatine was a lactim having the group $\begin{matrix}N=COH \\ | \quad\ | \end{matrix}$, and oxindol was a lactam with the group $\begin{matrix}HN-CO \\ | \quad\ | \end{matrix}$; carbostyril was a lactim, while oxypyridine and hydrocarbostyril were lactams. In preparing the

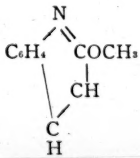
[1] Ber. d. chem. Gesell. **15**, 2093.

ethers the silver salts were sometimes used; frequently the alkyl halide was made to act on the sodium or potassium salt in alcoholic solution. It was supposed that the result would be the same whichever of these two methods was used. Friedländer,[1] in collaboration with Weinberg and afterwards with Müller, showed that, according to the method adopted, the lactam-ether (Fig. I) or the lactim-ether (Fig. II) could be prepared from carbostyril.

I.



II.



Friedländer suggested that other compounds may show a similar behavior. In looking over the literature up to that date, it is interesting and suggestive to see how the conclusions as to the structure of these compounds depended entirely on the method used in preparing the ethers. Isatine,[2] isatoxime,[3] and carbostyril were lactims; their ethers were prepared from the silver salts. γ-Oxyquinaldine,[4] oxynicotinic acid,[5] pseudo-lutidostyril[6] and oxindol[7] all gave ethers in which the alkyl group was joined to nitrogen; their ethers were prepared by the action of the alkyl halide and sodium alcoholate or an alcoholic solution of potassium hydroxide. It is especially interesting that ethyl-pseudoisatine-α-ethoxim,[8] from which Baeyer made ethyl-pseudoisatine, $C_6H_4\begin{cases}NC_2H_5\\ CO\end{cases}>CO$, was prepared with sodium alcoholate and ethyl iodide.

In this connection an experiment which we recently made is worth mentioning, though only indirectly bearing on the rest of this paper. Isatine was boiled in alcoholic solution with ethyl iodide and the theoretical quantity of sodium alcoholate for two hours. On boiling off the greater part of the alcohol and adding water, a dark resinous product separated; this product gave, after shaking out

[1] Ber. d. chem. Gesell. **18**, 1528, and **20**, 2009. [2] Baeyer and Oekonomedes: Ibid. **15**, 2093.
[3] Baeyer and Comstock: Ibid. **16**, 1704. [4] Knorr and Antrick: Ibid. **17**, 2870.
[5] v. Pechmann: Ibid. **18**, 317, and **17**, 2390. [6] Hantzsch: Ibid. **17**, 2903.
[7] Ibid. **16**, 1704. [8] Baeyer: Ibid. **16**, 2188.

with ether and evaporating the ether, a well crystallised body, but mixed with a considerable quantity of the resinous material. It was, however, easily purified by crystallising from boiling water. After a second recrystallisation it fused at 95°. The compound corresponds exactly to the description of ethyl-pseudo-isatine. It dissolves in dilute potassium hydroxide, giving a light yellow solution, from which it is precipitated at once unaltered on the addition of an acid. The compound, $C_6H_4\begin{matrix}N\\CO\end{matrix}\!\!>\!\!=COC_2H_5$, corresponding to the methyl ether obtained by Baeyer and Oekonomedes from the silver salt of isatine, should regenerate isatine under these conditions. We have no intention of entering into a discussion of the "tautomerism" of the groups CO — NH, HO.C = N, but would call attention to the fact that it is the tendency of a silver atom entering into such a compound to give it the form C.OH = N, even where the alkali salts are derived from the lactam form CO — NH.

One compound in which the group CO — NAg has been hitherto regarded as existing beyond question, has interested us on account of the iodine compound made from it: silver succinimide. We shall describe later on the action of iodine on silver formanilide, and the formation of the compound C_7H_6NOI, whose only analogue known thus far (at least as far as its formation is concerned) seems to be Bunge's[1] "iodo-succinimide," prepared by acting with iodine on silver succinimide. The formation of the compound C_7H_6NOI at ordinary temperature from silver formanilide makes it probable that the compound has the structure $C_6H_5N{=}C\!<\!\begin{matrix}H\\OI\end{matrix}$. The formation of iodo-succinimide under the same conditions led us to the idea that both iodo- and silver succinimide might be derivatives of the form

$$\begin{matrix}CH_2.CO\\|\\CH_2C.OH\end{matrix}\!\!>\!\!=N.$$

The experimental verification of this did not, however, work as smoothly as we had hoped. The results will be published at a later date.

Silver formanilide.—This salt can be prepared by dissolving the sodium salt in alcohol of about 50 per cent., and gradually adding the theoretical quantity of silver nitrate, also in dilute

[1] Ann. Chem. (Liebig), Suppl. **7**, 119.

alcoholic solution, stirring the solution well meanwhile. After the silver nitrate solution is all added it is advantageous to add more water and wash partly by decantation. The salt is white when first precipitated, but by the time it has been washed and dried it always has a gray color, light or dark according to the time used and its exposure to light. It is amorphous. A quicker method of preparing it is to dissolve the theoretical quantities of formanilide and silver nitrate in dilute alcohol, adding gradually the theoretical quantity of pure sodium hydroxide with constant stirring, and washing with water as in the other method. At ordinary temperature the salt is quite stable. Unless great care is used to avoid an excess of the alkali and to use pure alkali, the purity of the salt suffers.

A silver determination gave Ag = 47.89 per cent.; calculated for $C_6H_5N{=}C{<}^{OAg}_{H}$, Ag = 47.37 per cent.

Methyl-iso-formanilide.—When silver formanilide is treated with methyl iodide in molecular proportion, the iodide being diluted with a small quantity of perfectly dry ether, a thick paste is formed, or indeed, where the quantity of ether used is small, the liquid is entirely absorbed by a part of the salt while the rest looks perfectly dry. On standing for a time at ordinary temperature the appearance of the mixture gradually changes; it becomes more fluid, and after 24 hours the formation of silver iodide seems to be complete. When large quantities are used the reaction is accompanied by evolution of heat, sufficient to make the ether boil. More ether is now added and the liquid filtered from silver iodide. After boiling off the ether a heavy oil is obtained, the greater part of which boils from 195°–200°, and on redistilling, a colorless product, boiling at 196°–198°, results.

Analysis showed the composition C_8H_9NO.

	C_8H_9NO. calculated.	Found.
C	71.11	71.39
H	6.66	6.89
N	10.37	10.41

As to the structure of this compound there can be no question; it is represented by the formula $C_6H_5N{=}C{<}^{H}_{OCH_3}$.

The tendency of methyl-iso-formanilide to form diphenyl formamidine is marked; it is analogous to the behavior of the imido-

ethers and the iso-thio-anilides. When mixed with aniline in molecular proportion the mixture warms up and finally becomes solid. The amidine was purified by recrystallisation from alcohol.

The reaction is

$$C_6H_5N=C<^{H}_{OCH_3}+C_6H_5NH_2=$$

$$C_6H_5N=C<^{H}_{NHC_6H_5}+CH_3OH.$$

The same reaction takes place when aniline is added to methyl-iso-formanilide in the presence of a large quantity of water. A dilute solution of aniline hydrochloride converts it at once into the hydrochloric acid salt of diphenyl-formamidine. For the preparation of the amidine the addition of aniline is not necessary. If hydrochloric acid, strong or dilute, is added to methyl-iso-formanilide, diphenyl-formamidine hydrochloride is formed at once. This is easily understood in the light of the former reactions. The reaction takes place in two phases. The first change is represented by the equation,

$$C_6H_5N=C<^{OCH_3}_{H}+H_2O+HCl=$$

$$C_6H_5NH_2HCl+HCOOCH_3;$$

and, second, the aniline hydrochloride formed acts at once on unaltered methyl-iso-formanilide. In the first phase the reaction is exactly analogous to the behavior of benzylidene-aniline, $C_6H_5CH=NC_6H_5$, on treatment with acids. The formation of the amidine also takes place, though slowly, on exposing the iso-formanilide to moist air. In all cases the diphenyl-formamidine melted at 137°–138° after recrystallising from alcohol.

	$C_{13}H_{12}N_2$ calculated.	Found.
C	79.60	79.82
H	6.12	6.15
N	14.28	13.94

Analysis, a comparison of the compound with diphenyl-formamidine prepared by other methods, and the splitting off of aniline[1] by boiling with dilute alcohol, serve to establish the identity of the compound beyond question.

Action of iodine on silver formanilide.—When the finely pulverised silver salt is mixed with dry chloroform and one molecule iodine is added, the formation of silver iodide begins at once. If

[1] Ber. d. chem. Ges. **15**, 2450.

the iodine is dissolved in chloroform before it is added, the reaction takes place rapidly at ordinary temperature; but no harm is done by warming on the water-bath. In taking molecule for molecule of the silver salt and iodine, the chloroform solution retains the iodine color, but on adding an excess of silver salt it is colored amber-yellow. After filtering from the silver iodide the solution is concentrated, first on the water-bath, finally at ordinary temperature, by passing a current of dry air over it until quite a quantity of light yellow crystals has separated. These are washed with dry ether to free them from the mother-liquor and from a small quantity of reddish oil. The new compound can be recrystallised from ether or chloroform, but unless great care is taken to work quickly and avoid moisture there is a separation of iodine. Dry ether or pure acetone can be used in place of chloroform in making the reaction, but we obtained a better yield in using chloroform and working with small quantities. The best yield was 2.7 grams from 5 grams silver salt. On heating the compound decomposes with separation of iodine; the separation is less, the more slowly it is heated. After keeping for a time it also smells strongly of iodine, and iodine crystals can be observed. An iodine estimation gave 50.27 per cent. iodine. The theory for C_7H_6NOI requires 51.42 per cent. iodine. The iodine determination shows clearly that the compound is derived from silver formanilide, by the introduction of one atom of iodine in the place of silver. Bunge has shown that iodine does not react with sodium formanilide, in which the metal is united with nitrogen.

We have shown that in silver formanilide the metal is attached to oxygen. The ready formation of the new compound from silver formanilide at ordinary temperature, together with Bunge's observation, seem to warrant our conclusion that its structure is represented by the formula $C_6H_5N=C<^{H}_{OI}$. Perhaps the best name that can be given to it is iodo-iso-formanilide. Iodo-iso-formanilide is decomposed by water, but we have not attempted to study the products. No definite melting point can be given. When slowly heated the separation of iodine is not large, and the contents of the tube are melted at about 110°, but in this case a second compound, the result of molecular rearrangement, is formed.

Para-iodo-formanilide. — After heating iodo-iso-formanilide slowly and keeping the temperature for a few minutes at 115°,

then crystallising from water, we obtained this second body in fine white transparent needles melting at 109°–110°. An iodine estimation gave 51.13 per cent. iodine.

The theory for C_7H_6NOI requires 51.42 per cent. This same rearrangement can be effected by heating iodo-iso-formanilide for a few minutes with formic acid; indeed, on adding formic acid it dissolves, heat is evolved, and the new compound needs only to be crystallised from water. The new body is para-iodo-formanilide. To prove its identity we prepared para-iodo-aniline by the method described by Michael and Norton,[1] and made the formyl compound. By boiling *p*-iodo-aniline with a slight excess of formic acid for a few minutes, boiling off the excess of acid and crystallising from hot water, we obtained the formyl compound in long needles exactly like those obtained from iodo-iso-formanilide.

	Calculated for $C_6H_4I.NHCHO$.	Found.
Iodine	51.42	51.77

It dissolves easily in alcohol, methyl alcohol acetone, ether, chloroform and benzene, with difficulty in cold water, more readily in hot water. The melting point remained constant after repeated recrystallisations from water at 108°–109°.

This formation of para-iodo-formanilide from iodo-iso-formanilide suggests the reaction which Bender described.[2] From a compound whose structure Bender considered to be $C_6H_5N{<}^{Cl}_{COCH_3}$, he obtained by molecular rearrangement *p*-chlor-acetanilide.

Our conclusion as to the structure of iodo-iso-formanilide suggested a re-examination of a number of compounds in which it has been supposed that the halogen is united to nitrogen. The work is now under way in this laboratory, and the results will be communicated later.

Formation of carbanilide.—On dry distillation of silver formanilide a solid crystallised compound is formed. This is easily separated from the oily products by washing with alcohol, and can be obtained pure by recrystallising from alcohol. It turned out to be *s*-diphenyl-urea.

	$CO(NHC_6H_5)_2$.	Found.
C	73.59	73.32
H	5.66	6.00
N	13.20	13.43

[1] Ber. d. chem. Gesell. **11**, 108. [2] Ibid. **19**, 2273.

It fused at 231°–233°, corresponding exactly to a specimen of diphenyl-urea prepared according to Weith.[1] We also converted some of the diphenyl-urea, obtained from silver formanilide, into triphenyl-guanidine, which melted at 144°, so that its identity is certain. The reaction by which it is formed can be formulated:

$$2C_6H_5N=C<\begin{matrix}H\\OAg\end{matrix}=2Ag+CO+CO<\begin{matrix}NHC_6H_5\\NHC_6H_5\end{matrix}.$$

That carbon monoxide is formed we proved in the customary way. The formation of disubstituted ureas from silver salts of the formyl compounds seems to be general. On distilling silver form-para-toluide, and recrystallising the product from alcohol, we obtained dipara-tolyl-urea melting at 255°.

	Calculated for $CO<\begin{matrix}NHC_6H_4CH_3\\NHC_6H_4CH_3\end{matrix}$.	Found.
C	75.00	74.77
H	6.67	6.77
N	11.66	11.63

SHEFFIELD LABORATORY, NEW HAVEN.

DICHLOR-SALICYLIC ACID.

BY JOSEPH L. HECHT.

The literature upon this subject furnishes us with descriptions of four acids, supposed to differ in chemical and physical properties, which means, necessarily, a difference in constitution.

First, Cahours, as early as 1845,[2] called attention to a dichlor-salicylic acid, obtained by the chlorination of potassium salicylate. His description of the properties of the acid and salts is so meagre that little importance can be attached to this publication.

Second, Rogers in an inaugural dissertation (Goettingen, 1875) mentioned an acid similar in composition, obtained by conducting a calculated amount of chlorine into glacial acetic acid containing dissolved salicylic acid. The acid thus obtained melted, according to Rogers, at 224° C., and gave a barium salt containing five molecules of water.

Third, Smith[3] obtained a dichlor acid by chlorinating salicylic

[1] Ber. d. chem. Gesell. **9**, 821. [2] Ann. Chem. (Liebig) **52**, 340.
[3] Proc. Am. Phil. Soc., June 15, 1877, p. 69; also Ber. d. chem. Gesell. **11**, 1225.

acid dissolved in ethyl alcohol. It melted at 214° C., and gave a barium salt containing three and one-half molecules of water of crystallisation.

Fourth, William Pauli in an inaugural dissertation (Goettingen, 1878) described a dichlor-salicylic acid produced by conducting a calculated amount of chlorine through carbon disulphide containing a weighed amount of salicylic acid in suspension. He gave as the melting point 223°–225° C., and stated that it forms a barium salt containing six molecules of water.

Dr. Smith having had occasion to prepare dichlor-salicylic acid according to the method described by Rogers, found that it was identical with the acid prepared by chlorination of salicylic acid in alcohol. This having occurred, the question arose, do the differences claimed for these acids really exist? The matter was handed to me at this stage. It was evident that in three of the four cases the only difference in preparation was the solvent used; in the other case the salt was first formed and the chlorine then introduced. Therefore, in the three cases above referred to, if there is a difference, it must be due to the solvent; in the other case a difference must be caused by the influence which the presence of potassium in the molecule might have on the entering chlorine atoms. Would the solvents in the one case and the presence of potassium in the other so influence the substitution as to produce different dichlor acids? Taking this as the first step towards the solution of the problem, I proceeded in the following manner. First, the fact that the acid of Rogers had been prepared and thoroughly studied by Dr. Smith, and by him shown to be identical with the acid chlorinated in alcohol, made it unnecessary for me to repeat that work, the details of which are given in the articles cited above. The acid of Pauli, who gave as its melting point 223°-225° C., was made as described by him, viz. by conducting a calculated amount of chlorine into carbon disulphide containing salicylic acid in suspension. A solution of caustic potash was then added and the potassium salt thus formed. As this is much more easily soluble than the acid it can be easily separated from the oily liquid. This was done by means of a separatory funnel. The potassium salt was then decomposed by hydrochloric acid. The acid thus liberated, after filtration and washing, was boiled with an excess of barium carbonate, producing the barium salt. The chlorination produced both monochlor and dichlor-salicylic acids; hence I found mixed with the

barium dichlor-salicylate barium mono-chlor-salicylate, but was able to separate the two salts by fractional crystallisation, the barium dichlor salt being the more insoluble, and by repeated crystallisation it was obtained pure. This crystallised in large, almost colorless needles.

While this salt was being prepared I made the dichlor acid and barium salt according to the method of Smith, viz. by chlorination of salicylic acid in alcohol. The alcoholic solution of the acid thus formed was thrown into a large quantity of water, which caused the separation of the acid. After filtering and washing, the barium salt was formed and purified as in the preceding case. During the entire operation the salts of the two acids appeared to be identical. Samples of each were taken, and after drying in the air-bath were weighed and analysed with the following results: Of the air-dried salt prepared by Smith's method 0.2867 gram was taken; the loss on drying at 170° C. until constant weight resulted was 0.0330 gram = 11.51 per cent. H_2O. The anhydrous salt gave 0.1064 gram $BaSO_4$ = 0.0626 Ba = 21.84 per cent. Ba. Of the air-dried salt prepared by Pauli's method, 0.4127 gram lost on drying at 170° C. until constant weight was obtained 0.0468 gram = 11.34 per cent. H_2O, and gave $BaSO_4$, remaining after evaporation with H_2SO_4, 0.1542 gram $BaSO_4$ = 0.0906 Ba = 21.95 per cent. Ba. The theoretical percentages of barium and water required by a salt of the following composition, $(C_6H_3Cl_2OHCOO)_2Ba + 4H_2O$, are 22.06 per cent. Ba and 11.59 per cent. H_2O. Smith found three and one-half molecules of water, but on reference to his paper I find he dried the salt over calcium chloride previous to heating in air-bath. I may mention here, in the determination of water great care is necessary that the temperature does not exceed 170° C., otherwise an aromatic odor is developed which undoubtedly indicates a slight decomposition, and the loss in weight calculated as water is consequently erroneous. From the pure salts the acids were liberated and were repeatedly crystallised from a mixture of alcohol and water, from which they separated in the form of white arborescent needles. Portions of the crystallised acids were melted side by side and showed a constant fusing point of 214° C. Samples of each were also sublimed between watch-glasses, and the sublimates thus obtained melted likewise at 214° C. That no doubt might remain as to these being dichlor acids, a determination of the chlorine was carried out. Of the acid prepared by Smith's

method, 0.2210 gram burned with calcium oxide gave 0.3083 gram AgCl = 0.07619 gram Cl = 34.47 per cent. Cl.

Of the acid prepared by Pauli's method 0.2120 gram gave 0.2930 gram AgCl = 0.07255 gram Cl = 34.12 per cent. Cl. The theoretical amount of chlorine required by dichlor-salicylic acid is 34.25 per cent.

The acid of Cahours was next prepared. Potassium salicylate was made by treating a boiling solution of salicylic acid with potassium carbonate. The salt thus obtained was purified by crystallisation, after which it was dissolved in water and chlorine conducted through the solution until the precipitate ceased to form. This precipitate was potassium dichlor-salicylate. It was filtered and washed, then brought into solution by boiling water and the acid liberated with hydrochloric acid; after filtration it was boiled with barium carbonate. Through the barium salt thus formed I was enabled to obtain the acid in a pure state. I may also mention that I obtained here a barium salt of the mono-chlor acid, from which the dichlor salt was separated by fractional crystallisation, as in the preceding cases. In fact, all that was observed in connection with the salts of the acids prepared by the other methods was here also observed. From this salt the acid was set free by hydrochloric acid and recrystallised several times from a mixture of alcohol and water. On comparing the behavior of this acid with that of those prepared by the other methods, the same statement holds good that was made in comparing the salts of this acid with those of the acids prepared by the other methods. The acid of Cahours melted sharply at 214° C.

Later, I distilled samples of the acids mixed with calcium oxide and sand in the proportion of one part acid to three parts calcium oxide. The heat was so regulated that the mixture merely browned in spots. In the case of each distillation an oily liquid came over, which upon a reduction of temperature solidified to colorless needles. These needles melted at 43° C. and gave out the characteristic odor of dichlor-phenol of the constitution $C_6H_3\begin{cases}OH\ (1)\\Cl\ (2)\\Cl\ (4)\end{cases}$. It is evident that to produce this compound the original acids must have had the constitution represented by the formula $C_6H_3\begin{cases}COOH\ (1)\\OH\ (2)\\Cl\ (3)\\Cl\ (5)\end{cases}$.

Thus there no longer remains a doubt as to the positions of the chlorine atoms in the dichlor acids; they have the same constitution and are identical. I may also add that Lössner[1] found that when antimony pentachloride acted upon salicylic acid, a dichlor acid was formed which melted at 214° C. From the facts herein given I feel justified in concluding that at present we have *but one dichlor-salicylic acid*, the structural constitution of which is represented above. Its melting point is 214° C.

The above work was carried out under the direction of Dr. Smith, and it is to him I owe, in great measure, my success in arriving at the above conclusion.

University of Pennsylvania.

REVIEWS AND REPORTS.

The Electrolytic Dissociation.—Hypothesis of Svante Arrhenius.

In 1857, almost simultaneously, Williamson and Clausius put forward the hypothesis that, in the fluid state at least, the molecules of compounds are not stable, in the sense that they are persisting aggregations of the identical molecules which originally united to form them; on the contrary, it was assumed that these molecules in so far resemble living organisms that, while the external appearance remains unchanged, the constituents are constantly being cast off and replaced by new ones of the same kind, so that there must always be a few molecules in a state of *dissociation*. This hypothesis has been favorably regarded as an explanation of the possibility of the coexistence of two opposing reactions, like those of etherification and saponification, where it is left to the chance encounter of molecules to occasion the existence of water and ether, or of alcohol and acid; it has likewise been regarded as a plausible explanation of the readiness with which an electrolyte will obey the influence of currents so feeble that their energy should not suffice to decompose a single molecule whose atoms were held together by their full chemical attraction. But when, six years ago, the attempt was made by Arrhenius to give a quantitative expression to this hypothesis, and to apply it to the explanation of all the anomalies observed in the physical

[1] J. prakt. Chem. **13**, 431.

behavior of solutions, much latent hostility was called forth, and a general discussion was aroused, which has continued until the present time. It appears, however, to the reviewer that a point has now been reached where the burden of proof would rest upon the opponents rather than upon the supporters of the hypothesis. An analysis of this discussion, set forth in proper order, might prove both lengthy and confusing, and I therefore relegate a chronological list of the original papers to the end of this review and confine myself to a brief exposition of the hypothesis as it stands at present, and of the chief objections which have been raised to it.

The fundamental idea is this: In electrical conductors of the second class electricity can be *transported* only by electrically "active" molecules, *i. e.* those in which the electrostatic charges are not neutralised within the molecule; the *ions* are able to receive and transport charges, positive and negative respectively, as long as they are separated, but not when they are firmly knit into a neutral molecule. It follows that there can be no conduction without a pre-existent partial dissociation of the molecules, which may be occasioned either by heat or more generally by the presence of a foreign body, such as water. It is, for instance, a well known fact that some of the best conductors, like the strong acids, become insulators when freed from the last traces of water, while water itself is classed among the poorest conductors when free from impurities. The mechanism by which water, *par excellence*, should produce electrolytic dissociation, while alcohol and other solvents do not, has yet to be explained; it does seem strange that such an effect should be produced without a corresponding dissociation of the water, an idea which Arrhenius rejects or admits only to a minimal extent. However that may be, electrolytic dissociation is assumed to be a phenomenon precisely corresponding to gaseous dissociation and obedient to laws expressed by the same thermodynamic formulæ, with this difference, that "osmotic" pressure must replace gas pressure. Consequently, dissociation must be increased by dilution (increase of volume) and by heat; but for different substances the corresponding coefficients may differ.

1. The first application of this hypothesis affects Kohlrausch's law of conduction;[1] the conducting power of an electrolyte is no longer the sum of the velocities of all the ions, but of that proportion which are free to move. Only for extreme dilutions do we find a rigorous adherence to the equation $\lambda = u + v$, which becomes in less dilute solutions $\lambda = \alpha (u + v)$ (I), where α expresses the "coefficient of activity," or that proportion of the whole number of molecules which is dissociated. Experiments having given very reliable results for u and v in the case of quite a number of ions, and λ being known for a large number of compounds, at

[1] Compare this Journal **11**, 116.

various degrees of concentration, the respective values of a are readily obtained.

2. The number of molecules in the solution is increased by the dissociation. If each molecule is dissociated into k constituent ions, and n_1 molecules are thus broken up, while n remain associated, the osmotic pressure must correspond to the presence of $n + kn_1$ molecules, instead of $n + n_1$. We shall have for the relation of the true osmotic pressure to that calculated upon the assumption that the molecules remain intact, $i = \frac{n + kn_1}{n + n_1}$.

The definition of the coefficient of activity has introduced the value $a = \frac{n_1}{n + n_1}$, whence

$$i = 1 + (k - 1)a \quad \text{(II)}.$$

This explains the fact, alluded to in a recent review, that the molecular weight of an electrolyte, as determined by any of the "osmotic" methods, must be found smaller than theory would require. The coefficient i has been determined for many electrolytes, both by the freezing-point method and de Vries' and Hamburger's isotonism methods, and has in almost every case been found to agree astonishingly well with the corresponding value obtained from equation II, after calculating a by equation I. The few exceptions are found for salts which behave anomalously in other respects, and can be explained by making further assumptions which need not be discussed here.

3. If $k = 2$, that is if the electrolyte consists of but two ions, as in the case of monobasic acids and their salts with monovalent metals, the dissociation ought to obey the law which has been found to hold for gaseous dissociation where one molecule breaks up into two constituents, $\frac{p}{p_1^2} = \text{const.}$, p now referring to the *osmotic* pressure of the integral molecules and p_1 to that of either set of ions of the dissociated ones. The osmotic pressure depends upon the number of molecules in the unit volume of solution. Therefore, if we call the volume of the solution V, $p = \frac{n}{V}$, $p_1 = \frac{n_1}{V}$, and $\frac{n V}{n_1^2} = \text{const.}$

If the dissociation were complete, a result reached at infinite dilution, the molecular conductivity would reach a maximum value μ_∞, but at the finite dilution V, it has a smaller value μ_v, which is a measure of the number of dissociated molecules in the total. We can substitute in the last equation the values $n_1 = \frac{\mu_v}{\mu_\infty}$, and $n = 1 - \frac{\mu_v}{\mu_\infty}$, and obtain

$$\frac{\mu_\infty (\mu_\infty - \mu_v) V}{\mu_v} = C.$$

In this form the ratio has been examined by Ostwald, and has been found to remain practically constant for any one substance from ½ normal solutions up to the very highest dilutions amenable to experiment. For different acids, this constant assumes different values which have proved to be closely connected with the chemical activity of these acids. Putting $m = \frac{\mu_\infty}{\mu_v}$ and $K = \frac{1}{C}$, we can note for reference the equation to which Ostwald now reduces his results

$$\frac{m^2}{(1-m)V} = K. \quad \text{(III)}$$

4. If the solution of an electrolyte really contains free ions, how is it that this does not at once become apparent, either by the decomposition of water, or by some physical heterogeneity of the system? The answer lies in the further definition that these free ions bear equal and opposite electrostatic charges, which do not permit any local preponderance of one sort of ions over another, as this would mean a local accumulation of electricity in a system which is in equilibrium. Consequently—although the ions travel with different velocities—if they are travelling in the same direction as in diffusion, the attraction of their electrostatic charges compels them to accommodate their rates one to another, so that the slower ion is accelerated while the faster is retarded; the rate of diffusion of the salt is therefore intermediate between the velocities of the two ions. These conditions have received a rigorous mathematical formulation, and the close agreement between the theoretical and experimental result affords a beautiful confirmation of the fundamental hypothesis. (Nernst.)

5. Any cause, on the other hand, which produces a relative dislocation of the positive and negative ions must occasion electrical heterogeneity, showing itself by differences of potential at different points. Upon this idea a plausible "osmotic" theory of voltaic electricity has been based and substantiated by experiment. (Nernst.)

6. Conversely, any difference of electrical potential in the solution must produce a motion of the ions. Here we have the Clausius hypothesis of electrolysis. The introduction of electrodes disturbs the equilibrium of the solution, the positive ion moves to the cathode, where it gives up its charge, while the negative ion does the same at the cathode. It is only when the ions are relieved of their charges that they are capable of attacking the metal of the electrodes, or of decomposing water, causing the well-known secondary effects; charged, and in the paralysing presence of an opposite charge, they are supposed to be incapable of doing this. In this connection may be cited an experiment which appears incomprehensible unless free ions are assumed to exist in the solution. Dilute sulphuric acid, contained in a flask whose exterior was coated with tin-foil, was connected by a wick with a

Lippmann electrometer; upon giving a positive charge to the exterior of the flask the electrometer indicated the presence of positive electricity, and some bubbles of hydrogen were evolved near it. Consequently, the flask being a modified Leyden jar, negative ions (SO_4) had collected on the interior, while the corresponding hydrogen had been driven over toward the electrometer.

7. Properties like density, refractive power, capillarity and viscosity of saline solutions, whose numerical values appear to depend upon the sum of two factors characteristic of the acid and of the metal, should show this additive nature best where the salts are most dissociated; this appears to be the case.

8. We have now to consider the chemical side of the hypothesis, and we are met by the startling assertion that those acids show the greatest degree of dissociation which we consider the strongest. Indeed, according to Arrhenius, chemical activity depends upon the degree of electrolytic dissociation, only the dissociated molecules being capable of entering into reaction. A fundamental difference is hereby inferred to exist between reactions among electrolytes and reactions introducing only non-electrolytes, or, to recall antiquated notions, between reactions which involve substances of the water and hydrochloric acid types, and those involving merely the hydrogen and ammonia types. Valid objections raised to this distinction would upset the theory from the chemist's standpoint: examples in favor of the distinction have been adduced, such as the fact that the characteristic halogen reaction with silver nitrate is only shown by such compounds in which the halogen can be supposed to exist as a free ion, while with those which contain the halogen within the radicle, like trichloracetic acid, the reaction fails. Considering by themselves the reactions between electrolytes, it is noticeable that the presence of water or another solvent appears to be necessary (cf. the passivity of absolutely dry gases). The law of Guldberg and Waage must be modified in so far that the speed of reaction is not a function of the total masses of the electrolytes in solution, but of the masses of dissociated ions: vant' Hoff has introduced the coefficient i (isotonic coefficient) successfully enough into these considerations, and i has already been shown to be a function of α (II). In the acceleration or retardation of etherification and saponification, the acids and bases must act proportionately to their stages of dissociation, so that Ostwald's old affinity-coefficients must correspond with the values of k in equation III, which is also found to be true; for the same reason the effectiveness of weaker acids (non-dissociated) increases more rapidly for additional dilution than does that of stronger acids which are much nearer their limit. The evidence to be obtained from the study of the kinetics of chemical reaction all appears to favor the theory.

9. New ideas are introduced with regard to chemical equilibrium. The laws of dissociation, where gases are concerned, lead to the well-established postulate that dissociation shall be greatest where the atmosphere contains no excess of either of the constituents into which the molecule will break up; dissociation is unaffected by the presence of any other *indifferent* substances. By analogy, if a solution already contains a number of free ions of a particular sort, any substance consisting in part of this same sort of ions will not dissociate as fully as in pure water. Consequently an acid will be weakened by the presence of one of its neutral salts, but the effect will be much more perceptible for a weak acid than for a strong one. This has been verified by Arrhenius. Comparing, on the other hand, acids which have the positive ion H in common, a mixture of the two must affect their respective degrees of dissociation, unless before mixing the H had the same osmotic partial pressure in both solutions. This means that there shall be the same degree of dissociation in the two solutions, that they shall be "isohydric." Under such conditions, if m parts of one solution having the conductivity a be mixed with n parts of the other having the conductivity b, the resulting solution will conduct as if each electrolyte were conducting independently and unchanged. Its conductivity is $\frac{ma+nb}{m+n}$, no matter what the relative values of m and n are. Furthermore, if two solutions are "isohydric" with a third, they must be isohydrous with each other. These two consequences have been substantiated by the examination of the conductivity of mixtures of "isohydric" solutions of acids with one another and with those of their respective neutral salts, of neutral salts with one another and with the solutions of their respective bases, and finally of the bases with one another.

But if solutions are mixed together which are not "isohydric," the resultant conductivity will be greater than $\frac{ma+nb}{m+n}$, if calculation shows that the stronger acid is thereby partially reassociated and the weaker partially dissociated, while it will be less than the normal if the stronger acid is being dissociated and the weaker reassociated. This depends upon the fact that the dissociation of the same number of molecules produces a relatively greater effect when the acid is farther from the limit of dissociation which all approach asymptotically. In keeping with these facts is Nernst's observation that the solubility of a salt is decreased by the presence of compounds having a common ion with it; thus the solubility of silver acetate is equally affected by the presence of silver nitrate and sodic acetate.

10. The theory of "isohydric" solutions leads up to the important point of the neutralisation of acids by bases. In the first place, salts in dilute solutions are no longer considered to be the product of a reaction like the following:

$$KOH + HCl = KCl + HOH.$$

Where there is perfect dissociation, at extreme dilutions, the reaction is represented thus:

$$K + OH + Cl + H = K + Cl + HOH.$$

At greater concentrations this is accompanied by a certain reassociation of K + Cl and a dissociation K, OH and H, Cl, but K + Cl is supposed to be very small in all cases, as the dissociation of salts proves to be relatively very great. Neutralisation would therefore practically mean a formation of water from H and OH, and salts as such would only exist in concentrated solutions or as a combination of a very weak acid with a very weak base. A result of this would be that the heat of neutralisation in dilute solutions should be the same for all sorts of strong acids and bases, and should, in fact, equal that produced by the reaction H + OH, a very familiar fact. Mixtures of such salts should not be accompanied by a heat effect, which explains the phenomenon of thermo-neutrality. But a weak base or a weak acid introduces the positive or negative heat of dissociation pertaining to it; consequently the thermal effect of neutralisation must vary from that of H + OH, but this variation must decrease with the increase of temperature. If a stronger and a weaker acid are together mixed with a base, it is only the *weaker* anion which really *unites* with the metal, to a limited extent, while the stronger anion keeps the relatively greater amount of metal in electrolytic dissociation, *their* neutralisation being characterised by the union of their former conjugates H + OH. It is noticeable that electrolytic dissociation is to be sharply separated from the *hydrolysis* of sugars and of very weak salts like ammonic acetate, in which the reaction belongs rather to the class of non-electrolytes, although electrolytes are involved.

A final point with regard to chemical equilibrium is this, that when equilibrium has been reached in a solution containing a number of electrolytes, each one of these is in a state of dissociation, which depends upon the equilibrium of osmotic pressure between the non-dissociated molecules and all the free ions of the kinds which compose it. A distribution of metals and acids as it is usually assumed in older views is therefore rendered out of question, because a *free* ion belongs neither to one compound nor to another, it merely counterbalances that free ion of opposite charge nearest which it happens for the moment to be.

Having sketched Arrhenius' hypothesis, with some of its logical consequences, the task of judging it must be left to those readers who will compare the mass of experimental material and will convince themselves of the simple relations which the various phenomena appear to bear toward each other. As far as this test is concerned, the hypothesis will be found to fulfill its purpose. Shall it therefore be accepted?

The objections which have been raised are twofold, physical

and chemical. Prof. O. J. Lodge concedes the ingenuity and physical "orthodoxy" of the treatment, and it might appear that his criticisms to the earlier papers have been largely obviated by the further development of the theory; indeed they apply chiefly to points which I have omitted as no longer seeming essential to the theory, such as relations between the viscosity and the friction which a solvent opposes to the motion of the ions. But he appears mainly to object to the neglect of conduction by the solvent, which he believes would explain the rate of transference of the ions, without the assumption of unequal velocities of negative and positive ions. It is doubtful whether such an explanation would also elucidate the troublesome diffusion phenomena as well as does "dissociation" in the hands of Nernst. E. Wiedemann thinks that hydrates are the cause of better conduction, and explains osmotic anomalies by the assumption of a polymerisation of the solvent. Aside from Planck's proof, on thermodynamic grounds, that such polymerisation would not affect the vapor tension phenomenon in this way, in very dilute solutions, Ostwald pertinently asks why the electrolyte need cause a polymerisation which no non-electrolyte does.

The objections from a chemical standpoint have been chiefly raised by Prof. H. E. Armstrong, and are not all cogent. The following appear to be the most important at the present time:

1. Anhydrous hydrochloric acid and pure water do not conduct, while fused silver iodide does, which is an anomaly. Arrhenius finds an explanation in the dissociation of silver iodide by heat.

2. Hydrochloric, hydrobromic and hydriodic acids differ markedly in stability, but they are all assigned the same dissociation ratio. This is evidently a case of misapprehension, as the instability lies in the negative ion itself, and not in the compound.

3. Why does not alcohol dissociate electrolytes as well as water, and why does not water conduct?

4. According to Ostwald's measurements, phenylpropionic, cinnamic, and phenylpropiolic acids range in the order of their conducting power,

$$C_6H_5.C.C.COOH > C_6H_5.CH.CH.COOH > C_6H_5.CH_2.CH_2.COOH.$$

Therefore that acid is *most* dissociated which can *least* spare its hydrogen.

This argument illustrates the necessity of keeping the types of reactions apart. Nothing appears to justify his assumption that the carboxyl group should be affected in this way by what happens in a neighboring group, where hydrogen plays an entirely different rôle.

The main opposition to the dissociation hypothesis is to be found in a rival hypothesis which has found advocates in Mendelejew, Armstrong, Pickering, Crompton, Bonty and E. Wiedemann, the "hydration" hypothesis connected with the "residual

affinity" idea. Bonty holds that electrolytes are of two classes, those in which both ions show equal rates of transference, and the "abnormal" ones, in which this is not the case. All abnormal salts are said to be capable of forming hydrates and to do so. The law of equivalent ratio holds in so few cases, absolutely, that these considerations may be dismissed, in view of the more powerful ideas of Kohlrausch. E. Wiedemann argues from the change of color of salts of nickel, copper, cobalt, etc., upon dilution and heating, effects which Arrhenius ascribes to a difference in color between the free ion and the compound. Armstrong and Pickering present the "residual affinity" theory with much vigor. The atomic valences are not assumed to be whole numbers, so that it rarely happens that the positive and negative valences in a compound just balance. Consequently, a small residual affinity remains to each molecule, by virtue of which larger aggregations are formed, molecular compounds, either among the molecules of the same sort or with the molecules of the solvent. Armstrong's valences represent the old Berzelian negative and positive electricities, which cause their respective atoms to tend to opposite electrodes during the passage of the current, the atoms being set free by the complexes "straining" at each other as they pass each other. The idea of unequal electrical charges appears incompatible with Faraday's law that the current produces the same effect in all electrolytes. Pickering bases upon more modern ideas, separating affinity from electric charges, and sees in the phenomena of electrolysis and dilution effects of the dissociation and formation of various hydrates. The basis for this lies in the observation by Mendelejew, Pickering and Crompton, that various properties of acids and salts, such as conductivity, density, the heat of solution, when plotted as ordinates, with the percentage composition of the solution as abscissas, do not present regular curves. A study of their first or second differentials would appear to reveal the presence of points of abrupt change, and these points are supposed to represent definite chemical compounds. It does not appear that Arrhenius has entirely invalidated the proofs of the existence of such compounds, and there is no doubt that they present a very awkward obstacle to his theory which he has still to surmount. On the other hand, Pickering's explanations of the phenomena of freezing are extremely complex, and I am not aware of any positive attempt to explain facts like diffusion upon them. The thermo-chemical phenomena might be fairly explained by Pickering's reasoning.

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GRUNDRISS DER ALLGEMEINEN CHEMIE. Von W. Ostwald. Leipzig, 1889, Engelmann. pp. 402.

A sincere admirer of Professor Ostwald's monumental *Lehrbuch* must regret that the present text-book should have been chosen to present the recent developments of physical chemistry, rather than a second edition of the earlier, larger work. While the present volume is intended, according to the preface, to interest in physical chemistry those as yet unacquainted with the subject, it seems questionable whether this object can best be obtained by cutting away much that renders the larger work such delightful reading; nor does it seem plausible that a non-mathematical mind should grasp a mathematical formula better because the strict proof is omitted as too abstruse, and that the reader who is conversant with calculus should therefore be debarred from this aid to the comprehension. There is no doubt, however, that this little volume gives all the subject-matter proper of the two older volumes, with some additions; condensation has been obtained by employing smaller type, omitting many tables and much purely historical matter, and, finally, by omitting all references to titles of papers, instead of which the year of publication has been inserted in the text. The chapters have been rearranged into a very logical sequence, and the new points of view introduced by the hypothesis of osmotic pressure receive a very full and withal very comprehensible treatment.

For such as desire a rather hurried glance over a large field, this book can be very well recommended; but it is to be hoped that its presence in the chemist's library will not be supposed to atone for the absence of the Lehrbuch. M. L.